

Mathematical Analysis of Transport Properties of Polymer Films for Food Packaging. VI. Coupling of Moisture and Oxygen Transport Using Langmuir Sorption Isotherms

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Synopsis

Deterioration of food products stored in flexible packaging materials can be attributed to the presence of both water and oxygen in the environment surrounding the food. Mathematical models for the simultaneous permeation of moisture and oxygen through the packaging polymeric film and subsequent adsorption on the food surface are presented for the case of competitive adsorption of the two diffusing species. These models are then used to predict internal packaging conditions over time for selected food products. Oxygen and moisture permeation are treated as independent phenomena, and the competition is regarded as occurring on a surface described by the Langmuir adsorption isotherm. It is found that for certain polymer physical properties and relative surface coverages, water and oxygen molecules can dislodge each other from the food surface and, even for situations where the initial partial pressure of oxygen is less than the external partial pressure, can cause an outward flow of the more weakly adsorbed material. This theory is then extended to incorporate varying external conditions of storage.

INTRODUCTION

Storing food in a suitable environment can greatly extend its useful lifetime. One of the most practical methods of controlling the food conditions is through the use of flexible polymeric films for packaging which prevent the entry of substances that would cause the food to deteriorate.^{1,2} Typical packaging materials include cellulose acetate, polystyrene, polyethylene, polypropylene, and vinyl polymers such as poly(vinyl chloride) and poly(vinylidene chloride); recently ethylene vinyl alcohol copolymers have been also used for the same purpose. By using a thin film of one or more of these materials, an excellent light-weight barrier to the external environment can be created.

Besides noxious gases and liquids in the food's environment, moisture and oxygen, when present in excessive amounts, can cause the greatest rate of deterioration of a food product. Whether this deterioration is caused by physical or chemical means, a method for predicting the conditions inside the package (i.e., oxygen and moisture concentration) as a function of time could be of great use in optimizing packages for a particular food.

During food storage in packages, a series of undesirable phenomena occur which include permeation of moisture, oxygen, and organic vapors through the polymer film, moisture adsorption on the surface of the dehydrated

* Correspondence.

food,³⁻¹⁰ oxidation due to oxygen reactions with food components, enzymatic hydrolysis, and browning.¹¹⁻¹⁴ These undesirable phenomena are due not only to the transport properties of the polymer, but also to the special environmental conditions of the package during storage (i.e., due to the sorption characteristics of the food product). Technical analysis of the barrier properties of polymeric films has been reported by Salame and Steingiser,¹⁵ Masi and Paul,¹⁶ Brown and DeLassus,¹⁷ and Lee.¹⁸

Although extensive research has been carried out on the performance of various types of polymers for flexible packaging applications, very few mathematical models have been presented. The purpose of these models is to predict the so called "shelf-life" of a package, namely, the minimum time of storage before deterioration due to moisture or oxygen can occur. Labuza¹⁰ recently discussed several modelling efforts in the area of shelf-life determination, although most of his references are related to the sorption isotherms used to describe moisture sorption on foods and not to the actual problem of the prediction of the shelf-life from a combination of the sorption *and* diffusion mechanisms. The only true modelling efforts in this area have been presented by the groups of Labuza¹⁹ at the University of Minnesota, Karel²⁰ at MIT, and Peppas²¹⁻²⁵ at Purdue.

Past work by the groups of Peppas *et al.*²¹⁻²⁵ and Karel²⁰ has led to the prediction of *independent* moisture and oxygen levels inside a package as a function of time and polymer film permeability. The purpose of this contribution is to consider the *simultaneous, coupled* transport of moisture and oxygen through the film and onto the surface of the packaged food and to show some new interesting phenomena observed in packaged food products when both moisture and oxygen transport are considered.

THEORY

The environment surrounding a package consists of oxygen, nitrogen, water vapor, and very small amounts of other gases and vapors. When a gradient of concentration or partial pressure of any of these components exists across the packaging film, a multicomponent flux of the components occurs to reduce this gradient.^{7,10,13,22,26} In general, this diffusion of species is interdependent and must be solved by Stephan-Maxwell²² or generalized Fickian equations. Once the permeating species have penetrated through the packaging film, they are adsorbed on the surface of the food as described by a range of characteristic adsorption isotherms.^{7,13,22} The presence of the surface component can then initiate chemical reactions or physical degradation.²⁰

In the case detailed below, several simplifying assumptions have been made which, although restrictive, still allow accurate modeling of this transport phenomenon. These assumptions include (i) independent transport of moisture and oxygen through the packaging film; (ii) monolayer coverage of molecules on the food surface; (iii) energetically uniform surface; and (iv) slow chemical reactions or lack thereof. The first assumption holds true for relatively dilute diffusing systems using either hydrophobic or semicrystalline, hydrophilic polymers (i.e., for most cases of "real" packaging systems). The second and third restrictions are a result of the assumed Langmuirian adsorption isotherm, and are valid for nonporous food surfaces

such as those found in many freeze-dried or deep-fried foods.^{27,28} Indeed, monolayer coverage is inherently assumed in the derivation of most of the sorption isotherms used in food technology²² and for the early portion of the sorption behavior, which may correspond to water activities as high as $\alpha_w = 0.65$. The final assumption restricts the model to systems involving primarily physical deterioration or slow chemical reaction. This assumption needs further theoretical support. Several researchers, notably Karel, Labuza, and their collaborators,^{7,11,13,14} have discussed oxygen reactions with various components of the food product and they have proposed various kinetic expressions which can be applied over a specific range of water activities on the food product. Thus, kinetic expressions of first or higher order have been presented. Karel²⁷ has expressed the reaction rate of oxygen on many food products by a typical Langmuir-Hinshelwood kinetic expression, especially for slow oxidation reactions. He has used that same general expression in the most successful model published until now.²⁰ Thus, we have decided to adopt the same expression in the present work. Of course, our model would not be applicable in cases of fast occurring food oxidation.

Water Permeation

As in the past investigations by Peppas and his associates,²¹⁻²⁵ the flux of moisture (water) through a hydrophobic packaging film can be related to the internal and external water activities as follows

$$N_w = \frac{P_w p_w^\circ M_w}{RT} (\alpha_w^e - \alpha_w) = P'_w (\alpha_w^e - \alpha_w) \quad (1)$$

Here the subscript w refers to water, N_w is the mass flux of water through the film, P_w is the permeability of the film to water, p_w° is saturated pressure of water at the packaging temperature, M_w is the molecular weight of water, R is the gas constant, T is the packaging temperature, α_w^e and α_w are the external and internal water activities, respectively, and P'_w is the *effective permeability* of the particular film to water (consistent with the units of α). The reader should note that the term P_w incorporates the film thickness.

The external water activity is relatively constant in most packaging situations. However, the internal water activity changes with time until it equals the external water activity. It should be noted that the water activity is equivalent to the fractional humidity, which, if multiplied by 100, is the % relative humidity (% RH). The flux of water (moisture) can further be related to the amount of moisture on the inside of the package by a simple mass balance to yield

$$N_w = \frac{1}{S} \frac{dm_w}{dt} + \frac{p_w^\circ V_p M_w}{SRT} \frac{d\alpha_w}{dt} \quad (2)$$

Here m_w is the mass of water adsorbed on the packaged material, S is the surface area of the package, V_p is the unfilled volume of the package, and

p_w° is the saturation pressure of water at the packaging temperature. By combining Eq. (2) with Eq. (1) the following relation for the mass of water adsorbed as a function of time and water activities can be written.

$$\frac{d\tilde{m}_w}{dt} = \frac{P'_w S}{m_s} (\alpha_w^e - \alpha_w) - \frac{p_w^\circ V_p M_w}{m_s RT} \frac{d\alpha_w}{dt} \quad (3)$$

Here \tilde{m}_w is the mass of water per mass of food, m_s . Thus, the symbol \tilde{m} represents a type of surface concentration. In Eq. (3) it should be noted that the surface concentration of water increases if water is transported into the package by diffusion, and decreases if the water activity within the package increases due to desorption.

Oxygen Permeation

In a similar manner to that found in the previous section, the surface concentration of oxygen can be related to the internal and external partial pressures of oxygen as follows

$$\frac{d\tilde{m}_o}{dt} = \frac{P'_o S}{m_s} (p_o^e - p_o) - \frac{V_p M_o}{m_s RT} \frac{dp_o}{dt} \quad (4)$$

Here all the parameters are as defined before with the subscript o referring to oxygen, and p_o^e and p_o are the external and internal partial pressures of oxygen, respectively. This equation describes oxygen transport after packaging under low oxygen concentrations conditions.

Surface Competition

At this point in the modeling effort, Eqs. (3) and (4) are typically solved independently^{22,23} by assuming an applicable isothermal relation between the pressure or activity and the corresponding value of the normalized amount of water sorbed, \tilde{m} . In order to account for competition between the two adsorbing species, namely water and oxygen, an adsorption isotherm including both of the surface components must be derived. The surface adsorption is described by the Langmuir isotherm to quantitatively analyze some of the possible effects of surface competition. The development of the Langmuir isotherm arises from the steady-state equilibrium of adsorbing and desorbing species, and leads to such expressions for coverage as a function of partial pressure.

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad (5)$$

Here the term K represents an adsorption equilibrium constant, p is the partial pressure, and θ is the surface coverage of any species A . Extending

this expression to the present case we obtain

$$\theta_w = \frac{\tilde{m}_w}{\tilde{m}_{w,m}} = \frac{K_w \alpha_w}{1 + K_w \alpha_w + K_o p_o} \tag{6}$$

and

$$\theta_o = \frac{\tilde{m}_o}{\tilde{m}_{o,m}} = \frac{K_o p_o}{1 + K_w \alpha_w + K_o p_o} \tag{7}$$

where $\tilde{m}_{w,m}$ and $\tilde{m}_{o,m}$ are the monolayer coverages of water (subscript w) and oxygen (subscript o), respectively. Using the coupled isotherms presented in Eqs. (6) and (7), Eqs. (3) and (4) can be combined to yield a system of two first order linear differential equations in p_o and α_w . These equations are

$$\begin{aligned} \frac{P'_w S}{m_s} (\alpha_w^e - \alpha_w) = & \left[\frac{\tilde{m}_{w,m}(K_w + K_w K_o p_o)}{(1 + K_w \alpha_w + K_o p_o)^2} + \frac{p_w^o V_p M_w}{m_s RT} \right] \frac{d\alpha_w}{dt} \\ & - \left[\frac{K_w K_o \alpha_w}{(1 + K_w \alpha_w + K_o p_o)^2} \right] \frac{dp_o}{dt} \end{aligned} \tag{8}$$

and

$$\begin{aligned} \frac{P'_o S}{m_s} (p_o^e - p_o) = & - \left[\frac{K_w K_o p_o}{(1 + K_w \alpha_w + K_o p_o)^2} \right] \frac{d\alpha_w}{dt} \\ & + \left[\frac{\tilde{m}_{o,m}(K_o + K_w K_o \alpha_w)}{(1 + K_w \alpha_w + K_o p_o)^2} + \frac{V_p M_o}{m_s RT} \right] \frac{dp_o}{dt} \end{aligned} \tag{9}$$

We may represent the various terms appearing in these equations as follows:

$$A_{11} = \frac{(\tilde{m}_{w,m}(K_w + K_w K_o p_o))}{(1 + K_w \alpha_w + K_o p_o)^2} + \frac{p_w^o V_p M_w}{m_s RT} \tag{10}$$

$$A_{12} = - \frac{K_w K_o \alpha_w}{(1 + K_w \alpha_w + K_o p_o)^2} \tag{11}$$

$$A_{21} = - \frac{K_w K_o p_o}{(1 + K_w \alpha_w + K_o p_o)^2} \tag{12}$$

$$A_{22} = \frac{\tilde{m}_{o,m}(K_o + K_w K_o \alpha_w)}{(1 + K_w \alpha_w + K_o p_o)^2} + \frac{V_p M_o}{m_s RT} \tag{13}$$

$$B_{11} = \frac{P'_w S}{m_s} (\alpha_w^e - \alpha_w) \tag{14}$$

$$B_{21} = \frac{P'_o S}{m_s} (p_o^e - p_o) \tag{15}$$

Then Eqs. (8) and (9) can be combined in terms of the matrices **A** and **B** with matrix components as defined above to yield:

$$\begin{bmatrix} \frac{d\alpha_w}{dt} \\ \frac{dp_o}{dt} \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix}^{-1} \times \begin{bmatrix} B_{11} \\ B_{21} \end{bmatrix} = \mathbf{A}^{-1}\mathbf{B} \quad (16)$$

To find the water activity and oxygen pressure as a function of time, Eq. (16) needs to be numerically integrated over time. It should be noted here that to obtain these profiles from Eq. (16) the following food parameters must be specified: the adsorption equilibrium constants K_w and K_o , the monolayer surface concentrations $\bar{m}_{w,m}$ and $\bar{m}_{o,m}$ and the mass of the food, m_s . The first four parameters are available in classical food literature²⁸ and the food mass is usually defined by the user. In addition, the following packaging conditions need be specified: the package size, determining S and V_p ; the packaging material, defining P'_o and P'_w ; and the environmental conditions surrounding the package to define the temperature, α_w^e and p_o^e . Again, these values are supplied by the user.

DISCUSSION

In some of the more recent literature by Peppas and his associates,^{22,25} a single parameter, *the permeability sorption constant*, was defined which was used to characterize the entire sorption process and allow for easy package optimization. In the present context, however, the complex expressions arising from the surface competition do not allow the sorption to be governed by one parameter. For this reason, this discussion will center around the packaging of one particular food product, freeze-dried seafood, the physical constants of which are given in Table I. The values of the equilibrium uptake of oxygen and moisture on seafood are reported by Iglesias and Chirife.²⁸ The value of the Langmuir constant for oxygen was previously reported by Khanna and Peppas.²³ The value of moisture Langmuir constant was determined by fitting the data of Iglesias and Chirife²⁸ reported for freeze-dried seafood to a Langmuir isotherm and calculating by linear regression the best value of K_w . Other values specified for this packaging situation (and assumed arbitrarily, but using realistic values) include the package surface area $S = 129.03 \text{ cm}^2$, the unfilled package volume $V_p = 73.74 \text{ cm}^3$, the mass of the packaged food product $m_s = 30 \text{ g}$, the storage temperature of the package $T = 30^\circ\text{C}$ (86°F), the initial water

TABLE I
Sorption Constants For Freeze-Dried Seafood^{3,6}

$\bar{m}_{w,m}$	= 0.043 g/g
$\bar{m}_{o,m}$	= 0.076 g/g
K_w	= 32.42
K_o	= 50.00 MPa ⁻¹

activity = 0.15 (15% RH), and the initial oxygen partial pressure = 0.00149 MPa (0.0147 atm). This last value is the oxygen partial pressure *at the time of packaging* of the food product.

Constant Storage Conditions

Figures 1 through 4, show the prediction of moisture and oxygen change within a package which was stored in an environment consisting of a water activity equal to 0.70, (70% RH), and an oxygen partial pressure equal to 0.021 MPa (regular atmospheric conditions). The various curves represent different water and oxygen permeabilities. We will discuss the main characteristics of each figure both from a surface coverage and a packaging application point of view.

Figure 1 graphically details the effects of competition on the surface concentrations of water and oxygen. In curves P_1 and P'_1 , oxygen is shown to initially increase in coverage due to the diffusion of oxygen through the packaging film. However, after 25 days, the rate of coverage increase slows down because of the increased coverage of the more strongly adsorbed water. After 25 days, the oxygen coverage reaches a maximum, and then decreases as the water displaces the oxygen from the surface. By decreasing the water permeability by a factor of 5, 25, or 125 (shifting to curves P_2 , P_3 , or P_4), the maximum in oxygen coverage is shifted towards higher values. Hence the oxygen displacement, as well as the moisture permeation, occur at slower and slower rates.

For the same series of events, Figure 2 details the conditions within the package. By comparing Figures 1 and 2, it is evident that as the water forces the oxygen away from the surface, the partial pressure of oxygen within the package increases. Specifically, in the situation depicted by curve P'_1 , the oxygen displacement occurs so rapidly around 80 days that the

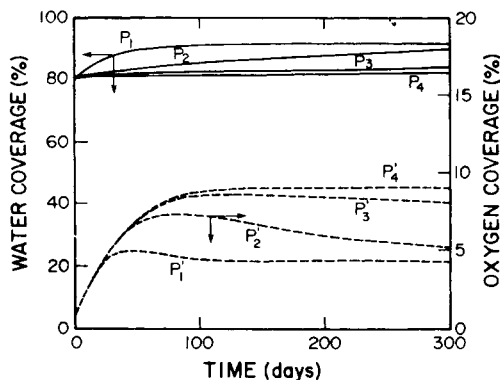


Fig. 1. Water and oxygen surface coverage percentages for freeze-dried seafood as a function of time for competitive Langmuirian adsorption. External water activity = 0.70; external oxygen partial pressure = 0.021 MPa. The initial conditions within the package were water activity = 0.15, and oxygen partial pressure = 0.00149 MPa. For all curves, the oxygen permeability of the packaging film is 1.6×10^{-6} cm/s. Curves P_1 - P_4 are profiles of water coverage for water permeabilities of 2.0×10^{-5} cm/s, 4.0×10^{-6} cm/s, 8.0×10^{-7} cm/s, and 1.6×10^{-7} cm/s, respectively. Curves P'_1 - P'_4 are the corresponding profiles of oxygen coverage for the above water permeabilities.

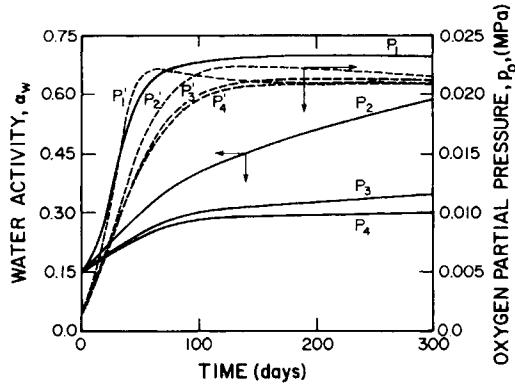


Fig. 2. Water activity and oxygen partial pressure within a flexible package for freeze-dried seafood as a function of time for competitive Langmuirian adsorption. External water activity = 0.70; external oxygen partial pressure = 0.021 MPa. The initial conditions within the package were water activity = 0.15, and oxygen partial pressure = 0.00149 MPa. For all curves, the oxygen permeability of the packaging film is 1.6×10^{-6} cm/s. Curves P_1 - P_4 are profiles of water activity for water permeabilities of 2.0×10^{-5} cm/s, 4.0×10^{-6} cm/s, 8.0×10^{-7} cm/s, and 1.6×10^{-7} cm/s, respectively. Curves P'_1 - P'_4 are the corresponding profiles of oxygen partial pressure for the above water permeabilities.

oxygen pressure in the package actually exceeds that of the external conditions. Therefore, after 80 days, oxygen actually diffuses out rather than in.

By decreasing the water permeability, the relative rate of oxygen diffusion out of the packaging film is faster, thus causing this increased outward flux of oxygen to maintain a lower value of oxygen partial pressure within the package. With respect to water activity in Figure 2, the high initial flux of oxygen causes the displacement of water, thus causing the inflection point in the water activity profiles at about 90 days (This is seen more noticeably

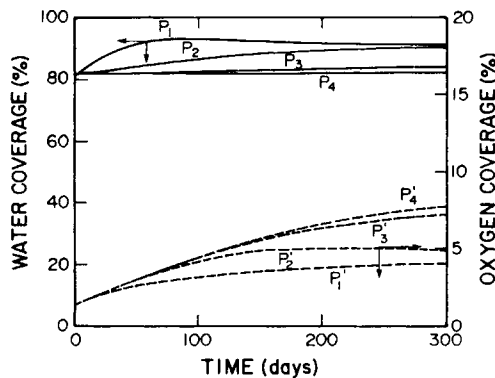


Fig. 3. Water and oxygen surface coverage percentages for freeze-dried seafood as a function of time for competitive Langmuirian adsorption. External water activity = 0.70; external oxygen partial pressure = 0.021 MPa. The initial conditions within the package were water activity = 0.15, and oxygen partial pressure = 0.00149 MPa. For all curves, the oxygen permeability of the packaging film is 3.2×10^{-7} cm/s. Curves P_1 - P_4 are profiles of water coverage for water permeabilities of 2.0×10^{-5} cm/s, 4.0×10^{-6} cm/s, 8.0×10^{-7} cm/s, and 1.6×10^{-7} cm/s, respectively. Curves P'_1 - P'_4 are the corresponding profiles of oxygen coverage for the above water permeabilities.

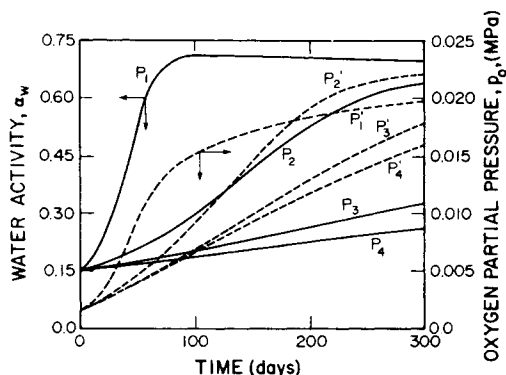


Fig. 4. Water activity and oxygen partial pressure within a flexible package for freeze-dried seafood as a function of time for competitive Langmuirian adsorption. External water activity = 0.70; external oxygen partial pressure = 0.021 MPa. The initial conditions within the package were water activity = 0.15, and oxygen partial pressure = 0.00149 MPa. For all curves, the oxygen permeability of the packaging film is 3.2×10^{-7} cm/s. Curves P_1 - P_4 are profiles of water activity for water permeabilities of 2.0×10^{-5} cm/s, 4.0×10^{-6} cm/s, 8.0×10^{-7} cm/s, and 1.6×10^{-7} cm/s, respectively. Curves P'_1 - P'_4 are the corresponding profiles of oxygen partial pressure for the above water permeabilities.

by comparing curves P_2 through P_4 .) The subsequent moisture transport is less noticeable, although still affected by the presence of oxygen.

Figures 3 and 4 present data obtained with the same water permeabilities as in Figure 1. However, the oxygen permeability was reduced by a factor of 5. The observed effect is a reduction of the rate of change of oxygen coverage and partial pressure. Generally, this effect is seen to shift the oxygen profiles to lower values, suppressing the effect of oxygen on the water profiles, and magnifying the effect of water on the oxygen profiles.

For the reader wanting to use the above results to optimize a packaging system, Figures 2 and 4 can be used to find either an appropriate shelf life, or a suitable packaging material. In either case, one would first determine the critical packaging conditions for the food product, the oxygen pressure and water activity beyond which the food is no longer acceptable. Then, by referring to the permeability curves for the particular packaging film, one is able to read off the corresponding time for the food's shelf life for the given critical conditions. Since the critical time for water will typically be different than that for oxygen, the actual shelf life will depend upon which species, water or oxygen, is most harmful for the particular food. To find the best packaging material, one starts with a specified shelf life requirement and refers to the critical packaging conditions. Then, by interpolating between curves, or figures if necessary, one can choose the desired oxygen and water permeability requirements for the package.

An Example

A polymeric film is to be used to package some typical predried seafood product. The critical water activity for the substance is 0.45 (i.e., at 45% relative humidity, the seafood becomes unacceptably humid, or perhaps rancid), and the critical oxygen partial pressure is arbitrarily set at 0.012

MPa. Storage and packaging conditions are identical to those presented before. It is desired to find

i. The shelf-life, given that the critical water activity is more important than the critical oxygen partial pressure, and Figure 5 presents the profiles for the given polymeric film.

ii. The water and oxygen permeabilities of a polymeric film to be used for storage of seafood for 40 days, given that the critical oxygen partial pressure is more important than the critical water activity, and Figure 5 presents the profiles for a known polymeric film.

The solution of this problem can be given in the following way

i. The critical water activity is the necessary packaging requirement. Hence, a horizontal line is drawn on Figure 5 at the critical water activity value of 0.45. Where this line intersects the water profile obtained for the permeability of the polymer selected for packaging, a second (vertical) line is extended to intersect the time axis. The corresponding shelf life is read as about 140 days for this particular polymeric film.

ii. In the second case, the critical oxygen partial pressure determines the packaging characteristics. Therefore, a horizontal line is drawn on Figure 5 at a hypothetical critical oxygen partial pressure of 0.012 MPa. We are also given that the shelf life is to be at least 40 days, hence a vertical line is extended upward from this value. The intersection of these lines represents the minimum required packaging conditions. Since the profile provided in Figure 5 lies below the required conditions, the permeabilities represented by Figure 5 will meet our requirements. From Figure 5, the water permeability is given as 4.0×10^{-6} cm/s, and the oxygen permeability is given as 1.6×10^{-6} cm/s. Then from typical permeability tables²⁴ we can select the appropriate polymer.

In the general case, a package may not be stored in a completely controlled environment. Daily fluctuations in humidity and temperature are a common occurrence. To monitor some of the possible effects caused by a changing

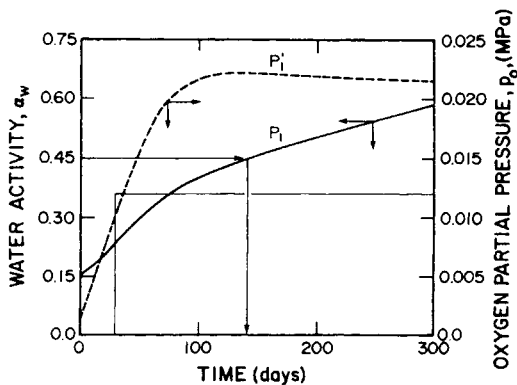


Fig. 5. Water activity and oxygen partial pressure within a flexible package for freeze-dried seafood as a function of time for competitive Langmuirian adsorption. External water activity = 0.70; external oxygen partial pressure = 0.021 MPa. The initial conditions within the package were water activity = 0.15, and oxygen partial pressure = 0.00149 MPa. The oxygen permeability of the packaging film is 1.6×10^{-6} cm/s, and the water permeability of the packaging film is 4.0×10^{-6} cm/s. Curve P_1 is the profile of water activity. Curve P'_1 is the corresponding profile of oxygen partial pressure for the above water permeability.

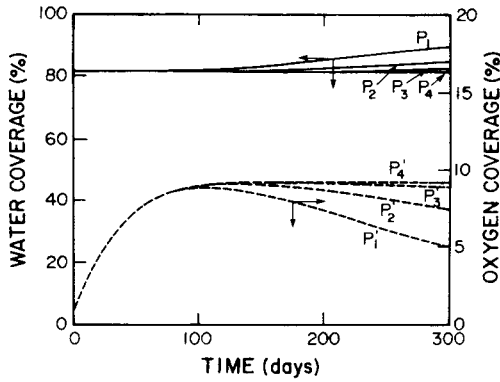


Fig. 6. Water and oxygen surface coverage percentages for freeze-dried seafood as a function of time for competitive Langmuirian adsorption. External water activity = $0.15 + 0.00183t$; external oxygen partial pressure = 0.021 MPa. The initial conditions within the package were water activity = 0.15, and oxygen partial pressure = 0.00149 MPa. For all curves, the oxygen permeability of the packaging film is 1.6×10^{-6} cm/s. Curves P_1 - P_4 are profiles of water coverage for water permeabilities of 2.0×10^{-5} cm/s, 4.0×10^{-6} cm/s, 8.0×10^{-7} cm/s, and 1.6×10^{-7} cm/s, respectively. Curves P'_1 - P'_4 are the corresponding profiles of oxygen coverage for the above water permeabilities.

environment, the simulated package discussed earlier was subjected to an environment (external storage conditions) where α_w^e changed linearly from 0.15 at day 0 to 0.70 at day 300, according to Eq. (17)

$$\alpha_w^e = 0.15 + 0.00183t \tag{17}$$

where t is in days. The results of this experiment are displayed in Figures 6 and 7. By comparison, the package stored in the varying environment does not show the effects of competition until the external water activity

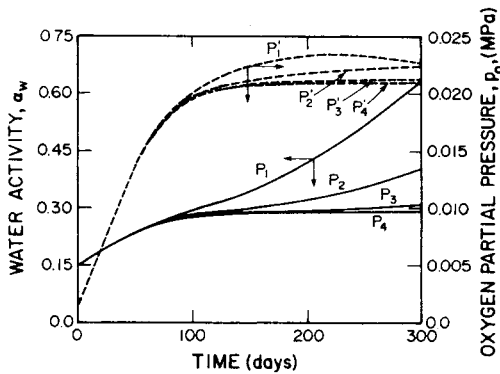


Fig. 7. Water activity and oxygen partial pressure within a flexible package for freeze-dried seafood as a function of time for competitive Langmuirian adsorption. External water activity = $0.15 + 0.00183t$; external oxygen partial pressure = 0.021 MPa. The initial conditions within the package were water activity = 0.15, and oxygen partial pressure = 0.00149 MPa. For all curves, the oxygen permeability of the packaging film is 1.6×10^{-6} cm/s. Curves P_1 - P_4 are profiles of water activity for water permeabilities of 2.0×10^{-5} cm/s, 4.0×10^{-6} cm/s, 8.0×10^{-7} cm/s, and 1.6×10^{-7} cm/s, respectively. Curves P'_1 - P'_4 are the corresponding profiles of oxygen partial pressure for the above water permeabilities.

has reached a high enough level to cause an appreciable flux of water into the package. At this point, the effects seen in Figures 6 and 7 are identical to those in Figures 1 and 2.

CONCLUSIONS

A mathematical model was presented to account for the possibility of competitive adsorption of water and oxygen on the surface of packaged food materials. This model was then used to simulate a packaging situation which was subsequently discussed from a physical point of view. In addition, the model was extended to the case of varying storage conditions.

References

1. A. L. Brody, *Flexible Packaging of Foods*, CRC Press, Cleveland, 1970.
2. T. R. Compton, *Additive Migration from Plastics into Food*, Pergamon Press, Oxford, 1980.
3. T. B. Labuza, *Food Technol.*, **22**, 263 (1968).
4. L. B. Rockland, *Food Technol.*, **23**, 1241 (1969).
5. T. P. Labuza, in *Theory, Determination and Control of Physical Properties of Food Materials*, C. K. Rha, Ed., Reidel, Dodrecht, Netherlands, 1975.
6. E. Rotstein and A. R. H. Cornish, *AIChE J.*, **24**, 956 (1978).
7. M. Karel, in *Theory, Determination and Control of Physical Properties of Food Materials*, C. K. Rha, Ed., Reidel, Dodrecht, Netherlands, 1975.
8. S. Mizrahi and M. Karel, *J. Food Process. Preserv.*, **1**, 225 (1977).
9. S. Mizrahi and M. Karel, *J. Food Sci.*, **43**, 750 (1978).
10. T. P. Labuza, *Food Technol.*, **92**, (April 1982).
11. T. P. Labuza, L. McNally, D. Gallagher, J. Hawkes, and F. Hurtado, *J. Food Sci.*, **37**, 154 (1972).
12. H. E. Chou and T. P. Labuza, *J. Food Sci.*, **39**, 479 (1974).
13. T. P. Labuza, *J. Chem. Educ.*, **61**, 348 (1984).
14. T. P. Labuza, *CRC Crit. Revs. Food Technol.*, 355 (1971).
15. M. Salame and S. Steingiser, *Polym. Plast. Technol. Eng.*, **8**, 155 (1977).
16. P. Masi and D. R. Paul, *J. Membr. Sci.*, **12**, 137 (1982).
17. W. E. Brown and P. T. DeLassus, *Polym. Plast. Technol. Eng.*, **14**, 171 (1980).
18. W. M. Lee, *Polym. Eng. Sci.*, **20**, 65 (1980).
19. T. P. Labuza, S. Mizrahi, and M. Karel, *Trans. ASAE*, 150 (1972).
20. M. Karel, *AIChE Symp. Ser.*, **132**, 107 (1981).
21. R. Khanna and N. A. Peppas, *SPE Techn. Papers (NATEC)*, 56 (1978).
22. N. A. Peppas and R. Khanna, *Polym. Eng. Sci.*, **20**, 1147 (1980).
23. R. Khanna and N. A. Peppas, *AIChE Symp. Ser.*, **218**, 185 (1982).
24. N. A. Peppas and G. S. Sekhon, *SPE Techn. Papers (ANTEC)*, **26**, 681 (1980).
25. N. A. Peppas and D. F. Kline, *Polym. Mater. Sci. Eng. Prepr.*, **52**, 579 (1985).
26. B. W. Hilton and S. Y. Nee, *Ind. Eng. Chem., Prod. Res. Dev.*, **17**, 80 (1978).
27. M. Karel, *J. Chem. Educ.*, **61**, 335 (1984).
28. H. A. Iglesias and J. Chirife, *J. Food Sci.*, **41**, 984 (1976).

Received November 7, 1985

Accepted January 7, 1986