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Modeling and Sensitivity Analysis of Mass Transfer in Active Multilayer Polymeric Film for Food Applications

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Abstract. The barrier performance of multilayer polymeric films for food applications has been significantly improved by incorporating oxygen scavenging materials. The scavenging activity depends on parameters such as diffusion coefficient, solubility, concentration of scavenger loaded and the number of available reactive sites. These parameters influence the barrier performance of the film in different ways. Virtualization of the process is useful to characterize, design and optimize the barrier performance based on physical configuration of the films. Also, the knowledge of values of parameters is important to predict the performances. Inverse modeling and sensitivity analysis are sole way to find reasonable values of poorly defined, unmeasured parameters and to analyze the most influencing parameters. Thus, the objective of this work was to develop a model to predict barrier properties of multilayer film incorporated with reactive layers and to analyze and characterize their performances. Polymeric film based on three layers of Polyethylene terephthalate (PET), with a core reactive layer, at different thickness configurations was considered in the model. A one dimensional diffusion equation with reaction was solved numerically to predict the concentration of oxygen diffused into the polymer taking into account the reactive ability of the core layer. The model was solved using commercial software for different film layer configurations and sensitivity analysis based on inverse modeling was carried out to understand the effect of physical parameters. The results have shown that the use of sensitivity analysis can provide physical understanding of the parameters which highly affect the gas permeation into the film. Solubility and the number of available reactive sites were the factors mainly influencing the barrier performance of three layered polymeric film. Multilayer films slightly modified the steady transport properties in comparison to net PET, giving a small reduction in the permeability and oxygen transfer rate values. Scavenging capacity of the multilayer film increased linearly with the increase of the reactive layer thickness and the oxygen absorption reaction at short times decreased proportionally with the thickness of the external PET layer.

Key words: active packaging, oxygen scavenger, inverse modeling, multilayer film

INTRODUCTION

The shelf life a food product in packaging material is considered safe if and only if the mass transfer of external materials like oxygen are kept as low as possible in order to preserve the quality and avoid the deterioration of quality attributes. Oxygen is one of the major factors for the deterioration of packed food products and its presence provides favorable environment for the growth of aerobic microorganisms, favors microbiological reactions, enzymatic reactions. This could cause adverse end effects such as loss of ascorbic acid in fruits and vegetables, oxidative rancidity of unsaturated fats, darkening and browning of fresh meat pigments, fostering the growth of aerobic spoilage microorganisms.

In recent years, active packaging materials have been the materials of choice over passive packaging materials due to their versatility and capability to preserve the food product and protect it from external influences that could cause deterioration. Polymeric films with the active materials inserted within the food product (i.e. scavenger sachets) have been used to keep the shelf life as longer as possible. In addition to sachets, oxygen-scavenging compounds can also be incorporated directly into the packaging material itself. These materials include flexible

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films, rigid plastics (injection or blow molded polymers) and liners in closures. The single layer film has also been used to package food products with the limitations of ingression of oxygen and relatively poor optical properties. The development of multilayer films has introduced a better barrier performance to achieve the desired packaging requirement according to the behavior of the food product subjected for preserving. On top of this, the inclusion of scavenger materials in multilayer films which is combined by the processes like, co-extrusion, lamination and coating will increase the barrier performance (Carranza et al., 2010, 2012; Solovyov and Goldman, 2006).

The addition of one or more reactive layers in the heterogeneous structure in packaging provides better barrier .properties in reducing permeation rates through the structure, compared to homogeneous barriers. Galdi et al, (2008) and Galdi and Incarnato (2010) have experimentally produced a multilayer films and evaluated the scavenging activity and influence of the different concentration of scavenger on the structure and barrier properties of active PET film. They reported that the PET film loaded with 10% AMS showed better oxygen scavenging capacity.

Recently, Di Maio et al. (2015) experimentally produced a three layer ABA type multilayer polymeric film (one reactive layer in the middle and two inert layers) by co-extrusion and studied the role of different mass ratio and layer thickness in controlling the scavenging capacity, activity time and oxygen absorption rate. They reported that the scavenging performance of the film linearly increases with the thickness of the reactive layer and the oxygen absorption reaction decreases proportionally with the thickness of inert layers. Therefore, the objective of this work was to develop the model to be used as a virtual lab to predict the barrier performance of the three layer polymeric film consist of two inert layers and one reactive layer in the center at different mass ratios with respect to their thickness. This model will also be used to analyze the effect of process parameters on the barrier performance.

MATERIAL AND METHODS

Model description

A multilayer polymeric film of thickness L and Area, *A*, composed of three layers (two inert layers and one reactive or scavenging layer) arranged in an alternating pattern was considered in this study. A one dimensional transient diffusion in a medium bounded by a container (vial) filled with air, in which all diffusing material enters through the plane faces and negligible amount through edges was assumed. At the beginning all layers of the film (active and inert layers) were assumed devoid of oxygen concentration while the active film was loaded with oxygen scavenging material at different mass ratios with respect to the thicknesses of the film subjected to this study.

Governing equations

The mathematical description of diffusion in an isotropic medium is based on Fick's first law (eq.1), which states that the transfer rate of diffusing substance through unit area is proportional to the concentration gradient normal to the section (Crank and Park, 1975).

$$J = -D\frac{\partial C}{\partial x} \qquad (1)$$

where J is the flux, D is the oxygen diffusion coefficient, C is the concentration of diffusant and x is the film thickness, [m]. Under unsteady state condition the three dimension general equation of the diffusion-reaction across a material can be written as:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) \pm R_A \qquad (2)$$

where C is the concentration of the diffusing material, x, y and z are the spacial coordinates, t, time and R_A is the rate of reaction considered. A one dimensional transient diffusion in the three-layer film was considered for this study. A material balance for the concentration of oxygen and scavenging material can be described by the following equations:

$$\frac{\partial C_{oxi}}{\partial t} = D\frac{\partial C_{oxi}}{\partial x^2} - k_b C_{oxi} C_{sc} \tag{3}$$

$$\frac{\partial C_{sc}}{\partial t} = -\nu k_b C_{oxi} C_{sc} \tag{4}$$

where C_{oxi} is the concentration of oxygen, C_{sc} is the concentration of scavenger material, k_d is the reaction rate constant, D is the oxygen diffusion coefficient, v is the stoichiometric coefficient for scavenging reaction, t is time and x is the position along the thickness. The oxygen diffusion coefficients were assumed constant for each layers, however, different values were considered since the presence of scavenger and reaction affects the permeability of oxygen into the film (Carranza et al., 2012). The reaction between oxygen and scavenger material was considered as second-order reaction and it was assumed that two molecule of oxygen reacts with one molecule of scavenger material. The diffusion of oxygen is much faster than the reaction kinetics since the thickness of the film is reasonably thin (Tung et al., 2012). The diffusion of gaseous permeating species into polymers can also depends on the molecular size, physical state of the diffusant and the morphology of the polymer and the solubility limit of the solute within the polymer matrix.

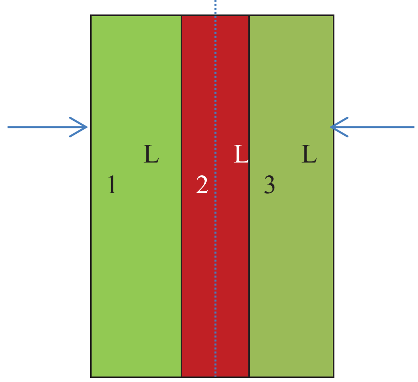

FIGURE 1. configuration of multilayer polymeric film used in model

Initial and boundary conditions

The concentration of scavenging material, C_{sc} in the inert layers is zero at all times and C_{sc0} in the active layer of the film. The initial concentration of oxygen in the vial is C_{oxi0} at time 0. The initial concentration of the scavenger in each film was dependent on the number of active sites in each film configuration.

The boundary conditions are listed below:

$C_{oxi}(0, t) = C_{oxi}(L,t) = C_{oxi0}$ Concentration of oxygen on both surfaces of the film

$$-D\frac{\partial C_{oxi}}{\partial x}\Big|_{x=0} = k_{coxi}(C_b - C_s)$$ Convective flux on the boundary of the film

$$\left.\frac{\partial C_{oxi}}{\partial n}\right|_{\left(L_1 + L_2/2, t\right)} = 0$$ Convective flux on the symmetry of the film

where k_{oxi} is convective mass transfer coefficient, C_b is bulk concentration of oxygen in the vial and C_s is the concentration on the interface of the film. The initial concentration of the oxygen in the vial was calculated according to the ideal gas equation at a temperature of 23°C and total pressure of 1 atm from which the partial pressure of oxygen is 0.21 atm.

The cumulative amount of oxygen permeated per unit area into the film through two external surfaces of PET can be expressed as:

$$Q = \int_0^t J\big|_{x=L} dt \tag{5}$$

where J is the flux, which describes the quantity of oxygen diffused across a unit area of the film per unit time, derived from first law of diffusion (Crank and Park, 1975):

$$J\big|_{x=L} = -\left(D \frac{\partial C_{oxi}}{\partial x} \right)\Big|_{x=L} \tag{6}$$

The oxygen concentration in a test vial can be calculated using the following equation as a function of time.

$$C_{oxi}(t) \cdot \mathrm{V}_{hs} = C_{oxi0} \cdot V_{hs} - Q(\mathrm{t}) \cdot \mathrm{A} \tag{7}$$

where V_{hs} is the head space volume of the vial, A is the surface area normal to the direction of diffusion into the film. *Q (t)*, the amount of oxygen permeated into the film at each time can be calculated from the flux.

Parameters and constants

Parameters and constants used in the model were taken from Di Maio et al. (2015).

Experimental

ABA type symmetrical structure (A and B represent the inert layers and the reactive layers respectively) polymeric films were considered for this study. Of the three layers, the middle layer was made up of PET polymer loaded with 10% of active material or scavenger while the external layers were pure PET. The active scavenger selected was Amosorb DFC 4020 (AMS, supplied by Colormatrix Europe, Liverpool, UK), a copolyster based polymer designed for production of rigid PET containers. The multilayer films at different mass ratio of scavenger concentration were produced in the laboratory according to the process and operating conditions described in (Di Maio et al, 2015). Monolayer films made of neat PET and active PET (10% wt AMS) were also considered in the study for comparison. The relative mass ratio of the co-extruded multilayer and monolayer films, with respect to their thickness (µm) are given in table 1.

TABLE 1 relative mass ratio and thickness of the layers (Di Maio et al., 2015)

Description	Relative mass ratios External layer/core layer	Thickness of the layers in µm
SL-PET	100/0	17.5/0/17.5
ML1	70/30	13.0/9.0/13.0
ML2	60/40	10.75/13.5/10.75
ML3	50/50	9.0/17.0/9.0

Simulations

One dimensional diffusion-reaction equations given in equation 3 and 4 were solved using finite element based software, COMSOL multiphysics (Comsol V. 5.0, Comsol AB, Stockholm, Sweden). A multiphysics module for transport of diluted species involving reaction was solved considering the initial and boundary conditions specified earlier in this paper. In order to analyze the influence of the film configurations and process parameters on the barrier performance of the films, parametric study was used for different thickness of the layers and parameters. The effect of different film thicknesses of inert and reactive layers, keeping the overall film thickness as constant, with respect to relative mass ratios of the loaded scavenger material was evaluated and compared with the experimental results. In addition, the effect of diffusivity and rate of reaction was also analyzed by varying the coefficients using the values reported in literature (Di Maio et al., 2015) as a base value. In addition to reaction–diffusion model in multilayer polymeric film, a simple diffusion model excluding the effect of oxygen scavenger (reaction) was also developed for similar film thickness and the values were analyzed and compared.

RESULTS AND DISCUSSION

Validation

The comparison of the concentration profile in the first configuration of multilayer film (ML1) from experimental result and from simulation were compared figure 2. Fast oxygen was observed in simulated result that followed by slow absorbing region before it reaches the plateau region. The first point, at which the plateau region and the scavenging activity attain constant, can be described as exhaustion time. During the first stage, diffusion occurs in the inert layers until linear profile of oxygen concentration gradient developed. The oxygen concentration in active layer shows gradual increase with time and remains uniform across the layer at infinite time when the scavenger concentration is completely diminished. In figure 3, the oxygen concentration profile in all three configurations and monolayer is shown. As it is clearly seen in the figure, the monolayer film without scavenging activity doesn't show any reactivity while the active films immediately react with the oxygen and reaches a plateau value based on configuration and composition of the multilayer films. This result agrees with Di Maio et al. (2014) in which they pointed out the activity of the PET film will end when the film absorbs all concentration and reaches plateau value after certain time interval.

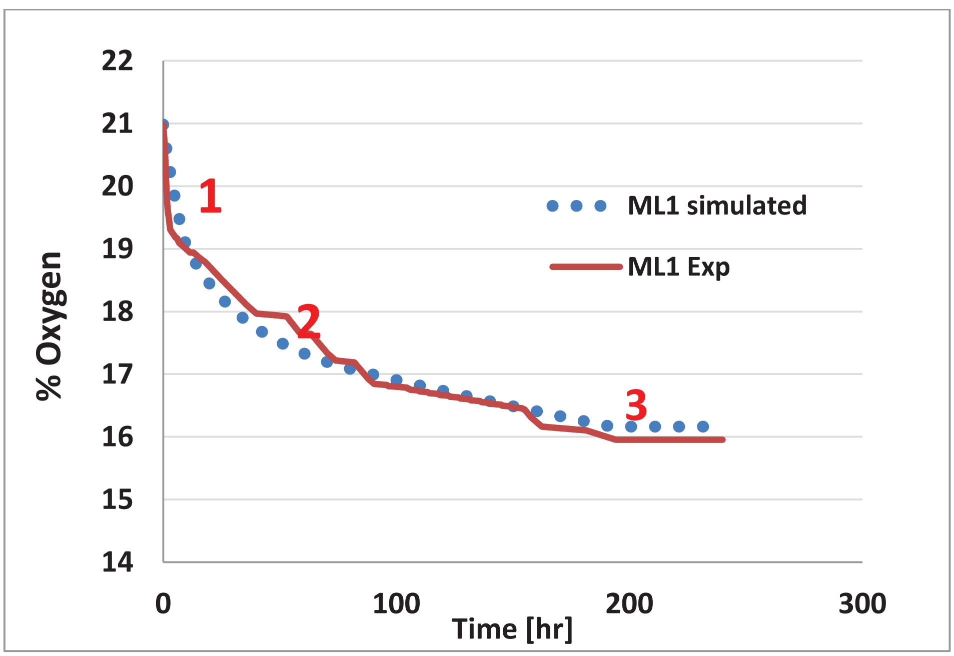

FIGURE 2. Model validation: comparison of experimental and simulated oxygen concentration profile in the ML1 configuration.

Effect of layer configuration on the diffusion and reaction

The permeability of a multilayer film is highly dependent on the thickness of the layers and the relative mass ratios of the material loaded in the film. In figure 3, it can be observed that the permeability of the gas decreases as the thickness of the layer increases. It should be noted that, the mass ratio of the scavenger concentration loaded in the matrix also determines the barrier performance. The higher the mass ratio, the longer the time it takes to reach concentration plateau. The multilayer configuration having the reactive layer in the middle will decrease the flux plateau of the oxygen diffused into the layer. As Carranza et al. (2012) also described, very long duration of and moderate flux plateau could be achieved by using inert layer prior to reactive one in the configuration. But, this could not be safe since the reactive layer will be in contact with the food product. The concentration of scavenger in reactive layer decreases gradually as reaction is going on and reaches the minimal value when it is completely diminished.

The configuration of three layers is preferable since the reactive layer placed in the middle decrease the flux plateau of oxygen due to the reaction kinetics. In this region, increasing the thickness of the reactive layer increases the time lag to be achieved.

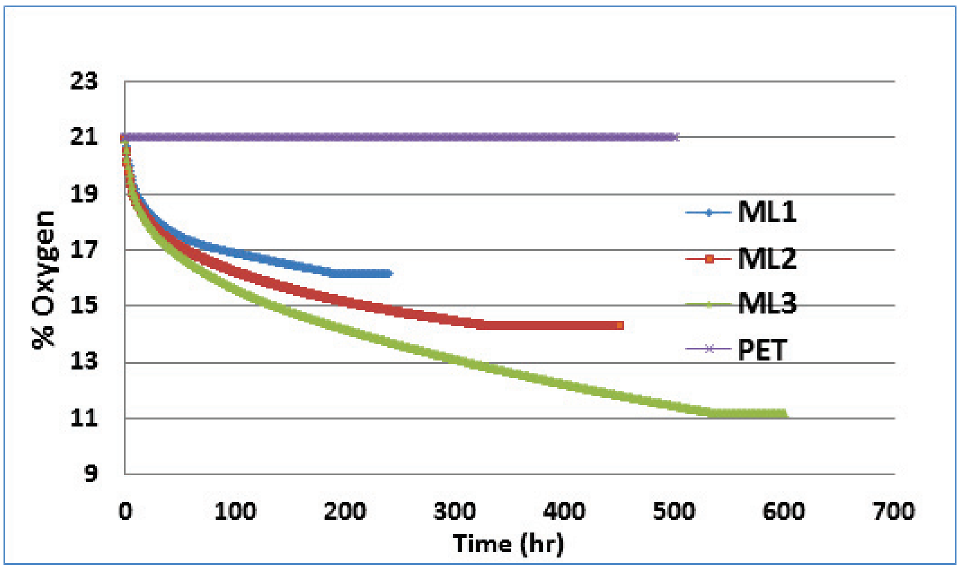

FIGURE 3. Oxygen concentration in the vial for all three configurations and monolayer film

Effect of scavenging concentration

The scavenging activity in the active layer is mainly dependent on the amount of scavenger concentration loaded in the matrix. In other word, the number of active sites found in the matrix of the film. This characteristic was determined by backward modeling technique using experimentally measured values reported in Di Maio et al. (2015) and Galdi et al. (2008). It is obvious that the larger the thickness of the inert layer the higher the number of active sites.

As shown in figure 4, the profile of oxygen permeation in the first multilayer configuration (ML1) is faster at the beginning (almost no scavenging activity) and concentration of oxygen tends to decrease as the scavenging activity starts at the boundary of the active film. The larger area of the film exposed to the oxygen concentration also influences the barrier property of the film.

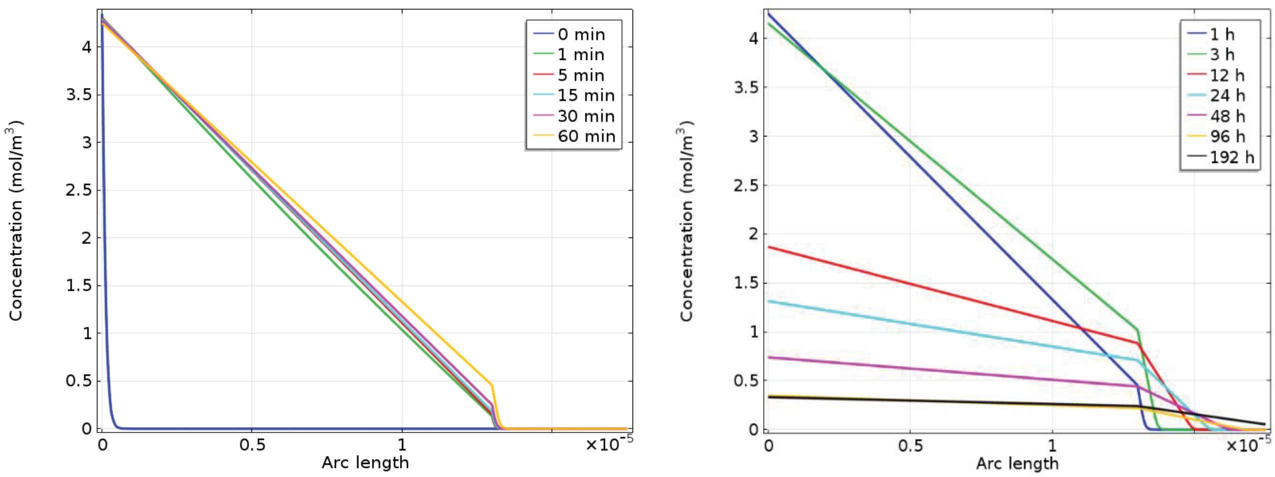

FIGURE 4. Oxygen concentration profile in the film matrix of ML1 configuration:
a) The first one hour permeation b) Different time intervals

CONCLUSIONS

Scavenging capacity of the multilayer film increases linearly with increase of the relative layer thickness and the oxygen absorption reaction at short times decreases proportionally with the thickness of the external PET layer. The results of the model show that, multilayer films incorporated with reactive layer slightly modify the steady transport properties in comparison to pure PET. As a result, the oxygen transfer rates and permeability were also reduced.

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