DESIGN OF PLASTIC MULTI-LAYER STRUCTURE THAT FIT THE REQUIREMENTS OF A SPECIFIC FOOD OR BEVERAGE

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Abstract

This paper presents a model that allows the determination of the permeability values of plastic multi - layer structures that may be coextruded, extrusion coated or laminated that fit the requirements of a specific food or beverage. The model includes the use of several data bases like plastic permeability data, food and beverage data related to maximum gain or loss of gases and plastic raw material costs.

The computational algorithm combines automatically different polymers predicting possible multi – layer structures based on adhesion criteria, maximum number of layers and the achievement of food requirements. The different calculation routines in the model include pressure, temperature and relative humidity corrections, change of units, among others.

The model predicted permeability values are compared against measured multi –layer structures for several barrier films, specifically, OTR and WVTR values.

Introduction

It is well known that the major consumption of plastics worldwide is directed to packaging applications: 38% in USA and 37% in Europe for the year 2001. One driving sector in packaging is food and beverage (1). The main requirement in this sector is to guarantee the product's organoleptic quality for the end consumer during a determined shelf life. Plastic packaging should minimize environment/package and product/package interactions and degradation reactions leading to loss of product quality: nutritional contents, aroma, taste, freshness, color, etc.

The primary concern in food and beverage packaging business is to respond quite accurately following questions:

1. Which are the allowed gas barrier properties for a product/package type to guarantee the product quality in a required shelf life ?
2. How should the plastic package be designed considering a multi-layer structure in such a way that the package fits the product requirements at reasonable costs ?

A model that allows the determination of the permeability values of plastic multi - layer structures that fit the requirements of a specific food or beverage can help for answering previous questions. The theory and model to be presented are applied to coextruded, extrusion coated or laminated plastic films.

Following factors are strongly considered:

- Food or beverage environmental or storage conditions
- Package characteristics
- Product shelf life and other critical conditions
- Selection of polymeric materials
- Selection of the maximum number of layers in the package structure
- Thickness range (min. and max.) for the design of the multi-layer film structure

Developed Model

Determination of the product maximal permeability

In general food and beverage have important composition and physical changes in contact with water vapor and gases, such as, oxygen, carbon dioxide, carbon monoxide, etc., considering the most relevant, water vapor and oxygen. In this paper the interactions environment/package and product/package will be examined taking into account polymer and product mass transfer behavior.

The maximum gain or loss of gases for a food product means the maximum gas quantity that can be entering or leaving the package before product damage or organoleptic changes are observed. Table 1 shows some typical allowed oxygen gain values for some food and beverage products. The presence of oxygen in the product promotes oxidation reactions and significant changes in aroma and taste. With this value, the calculation of the maximum allowed permeability to guarantee a determined shelf life is possible (2).

$$\left[\frac{P}{x}\right]_{Gas\max} = \frac{V_{gas}}{\theta * A * (P_2 - P_1)} \qquad (1)$$

and,

$$V_{gas} = \frac{G * W_{prod}}{\rho_{gas}} \qquad (2)$$

In the particular case of water vapor, the maximum allowed permeability is calculated quite different, since for any kind of product that gains or loses moisture, the moisture content is a function of the relative humidity, or water activity. From this information, a moisture isotherm can be obtained. The product sorption isotherms show moisture gain and the product desorption isotherms show moisture loss, see Figure 1. The presence of moisture in the product promotes hydrolysis reactions, growth of microorganisms or bacteria, loss of organoleptic properties, etc. The calculation of the maximum allowed permeability for water vapor to guarantee a determined shelf life is the following (3):

$$\left[\frac{P}{x}\right]_{vapor\max} = \frac{Ln\left(\frac{m_e - m_i}{m_e - m_c}\right)}{\left(\frac{A}{W_{prod}}\right) * \left(\frac{P_v}{b}\right) * \theta} \qquad (3)$$

Determination of the permeability of a plastic multi-layer structure

If a determined product (food or beverage) must be protected from gases or water vapor, the developed plastic package must satisfy the barrier condition in the following form:

$$\left[\frac{P}{x}\right]_{Total_i} \leq \left[\frac{P}{x}\right]_{\max_i} \qquad (4)$$

Every polymer offers different barrier properties depending on gas or vapor type, macromolecular structure, temperature and relative humidity. Therefore a multi-layer package requires various layers of different polymers (polar and non polar) to fit the required barrier conditions. Polar plastic materials are typically good gas barrier while non polar plastic materials are good barrier to water vapor. The calculation of the total permeability of a multi-layer structure is defined after equation 5. In this equation the index i is related to the gas or vapor permeating through the plastic multi-layer film (2,3):

$$\left[\frac{P}{x}\right]_{Total_i} = \frac{1}{\sum_{j=1}^{n}\left(\frac{x_j}{P_j}\right)_i} \qquad (5)$$

Correction for change in permeability with temperature.

Since the permeability coefficient changes with temperature, its value should be obtained at the storage or shelf conditions of the multi-layer package/product. In general the gas permeability coefficients are reported in the literature at 23^{o}C y 0% RH while the water vapor permeability coefficients are measured at 37.5^{o}C and 90% de RH (4,5,6,7,8). In general the permeability coefficients should be given at STP conditions (1 atm and 0^{o}C) for comparison purposes. The relationship for the temperature correction follows Arrhenius rule (2,3).

$$P_j = P_{j_o} * e^{\frac{E_j}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)} \qquad (6)$$

Correction for change in permeability with relative humidity (RH)

Polar polymers are subjected to change in permeability with relative humidity. In the case of these polymers in external or internal layers (in food contact), a polynomial regression is taken based on experimental data. The permeability coefficients are corrected at the storage or shelf conditions of the multi-layer package/product. If the polar polymers are placed in intermediate layers, the relative humidity influencing the polymer should be calculated based on the water vapor permeability of the adjacent layers as it is shown in equation 7, (9).

$$RH_j = RH_{OUT} - \left[\left(\sum_{j=1}^{n-1}\frac{x_j}{P_j} + \frac{x_n}{2 * P_n}\right)\left(\frac{RH_{out} - RH_{in}}{\sum_{j=1}^{n}\frac{x_j}{P_j}}\right)\right] \qquad (7)$$

Formation of multi-layer structures

The computational model generates multi-layer structures considering the number of desired layers (n) and the polymeric material selection (m) intended for the package design. The calculation uses an statistic combination of m materials and n layers satisfying following criteria:

- Compatibility between polymeric materials to be combined: if the compatibility is not guaranteed then a tie layer is included in the structure between two incompatible polymers.
- External and internal layers of the package are selected based on the thermal sealability behavior of the polymer and water vapor permeability.
- Hygroscopic polymers are always placed in intermediate layers of the film structure.
- The given maximum number of layers in the package structure should be considered
- The given thickness range (minimum and maximum) for the design of the multi-layer film structure should be checked.

Validated multi-layer film structures

The accepted and validated film structures satisfy food and beverage requirements implied in equation 4 and the previous mentioned criteria. In addition to there is a function to minimize the film cost per package area in square meter for each generated structure:

$$Cost = \sum_{j=1}^{n} \left(\rho_j * C_j * x_j \right) \quad (8)$$

Experimental

Plastic films

Several multi-layer film structures were measured and model simulated.

<u>Low and medium barrier laminated film structures</u>:

PET (12 µm)/PP (38 µm)
PET (12 µm)/PP (33µm)
BOPP (25µm)/BOPP(25µm)
BOPP (20µm)/BOPP PEARL (30µm)
BOPP (20 µm)/BOPP (20µm)
PET (12µm)/PP WHITE (51 µm)
PET (12 µm)/BOPP PEARL (30 µm)
BOPP (17.5 µm)/BOPP METALLIZED (17.5 µm)

<u>High barrier coextruded film structures:</u>

PA (46 µm)/EVOH-F (8 µm)/PP (28 µm)/PE-m (25 µm)
PP (18 µm)/EVOH-F (4 µm)/PP (18 µm)
PE (21 µm) / EVOH-L (4 µm) / PE (16 µm)

In this case EVOH F has an ethylene content of 32 %, while EVOH L has an ethylene content of 27 %.

Equipment

The permeation equipment for measuring the different plastic film structures is listed below:

WVTR - BRUGER GDP-C
Volume : 375 mm^3
Gas flow : 100 cm^3/min
Transmission area: 78.4 cm^2

OTR - MOCON OXTRAN 100
Gas flow: O_2 : 10 (cm^3/min)
N_2 : 15 (cm^3/min)
Transmission area: 20.3 cm^2
Partial pressure of O_2 : 0.1568 bar

Standards

The WVTR and OTR measurements were carried out following international standards.

WVTR		
Standard	CONDITIONS	EQUIPMENT
DIN 53380 II	40ºC –90% RH	Bruger GDP-C

OTR		
Standard	CONDITIONS	EQUIPMENT
ASTM D3985-95	23ºC –0% RH	MOCON , OXTRAN 100

Results and discussion

Experimental permeability data were compared with model calculated data for several film structures. The experimental data were corrected for changes with temperature and relative humidity.

Table 2 shows the experimental and obtained results for water vapor permeability for various laminated films. It can be observed that there is very good agreement between experiments and calculated data.

Table 3, Table 4 and Table 5 show the experimental and model calculated results for oxygen permeability including different type of barrier films. Low, medium and high barrier film structures were analyzed. It can be clearly observed that the low barrier films show the highest deviation between measured and calculated data. Medium barrier films show less deviation than low barrier films and finally, high oxygen barrier films show a very good agreement with the model calculated data. The high deviation for low oxygen barrier films can be maybe explained considering the high precision cell of the OTR equipment adequate for high barrier measurements.

Conclusions

According to the present study, it could be demonstrated that the developed computational model is a valuable tool for predicting the permeability values of plastic multi - layer structures satisfying the requirements of a specific food or beverage. The calculated values have a good accuracy for water vapor permeability and for oxygen permeability in a wide variety of films. The use of the computational model enhances multi-layer packaging design and it is an excellent alternative for film processing, film converting and food and beverage companies.

Nomenclature

$\left[\frac{P}{x}\right]_{Gas\max}$: Maximum allowed permeability for a gas [ml/(m^2.day.atm)] .

$\left[\frac{P}{x}\right]_{Vapor\max}$: Maximum allowed permeability for water vapor [g/(m^2. day.atm)].

V_{gas} : Gas volume entering or leaving from the package [ml].

θ : Shelf life [days].

A : Exposed packaging surface area [m^2].

P_2 : Gas partial pressure outside the package [atm].

P_1 : Gas partial pressure inside the package [atm].

G : Allowed gas gain or loss [mg of gas/g of product].

W_{prod} : Product weight [g].

ρ_{gas} : Gas density [g/ml].

m_e : Product humidity at equilibria [g water/g product].

m_i : Initial humidity of the product [g water/g product].

m_c : Critical humidity of the product [g water/g product].

P_v : Water vapor pressure [atm]

b : Secant slope of sorption or desorption isotherm between m_i y m_c [g water/g product].

$\left[\frac{P}{x}\right]_{Total_i}$: Total permeability of the multi-layer structure for a gas or vapor i

$\left[\frac{P}{x}\right]_{max_i}$: Maximum allowed permeability for a gas or vapor i

x_j : Thickness of j-layer in the structure [μm]

P_j : Permeation coefficient of the polymer in j-layer [ml. μm/(m^2. day.atm)].

n : Number of layers

P_{j_o} : Permeation coefficient at temperature of reference in j - layer [ml. μm/(m^2. day.atm)].

T : Storage temperature or any desired temperature [K].

T_o : Temperature of reference [K].

E_j : Energy of activation in j - layer [J/mol].

R : Value of the gas constant [8,314 J/(mol. K)].

RH_j : Average relative humidity in j - layer

RH_{OUT} : Relative humidity outside the package.

RH_{IN} : Relative humidity inside the package.

ρ_j : Density of the polymer in the *j* – layer [kg/m^3]

C_j : Cost of the polymer in the *j* – layer [US$/kg]

$Cost$: Total cost of multi – layer structure [US$/m^2]

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Key Words

Permeation, Plastic films, Oxygen barrier, Water vapor barrier, food and beverage

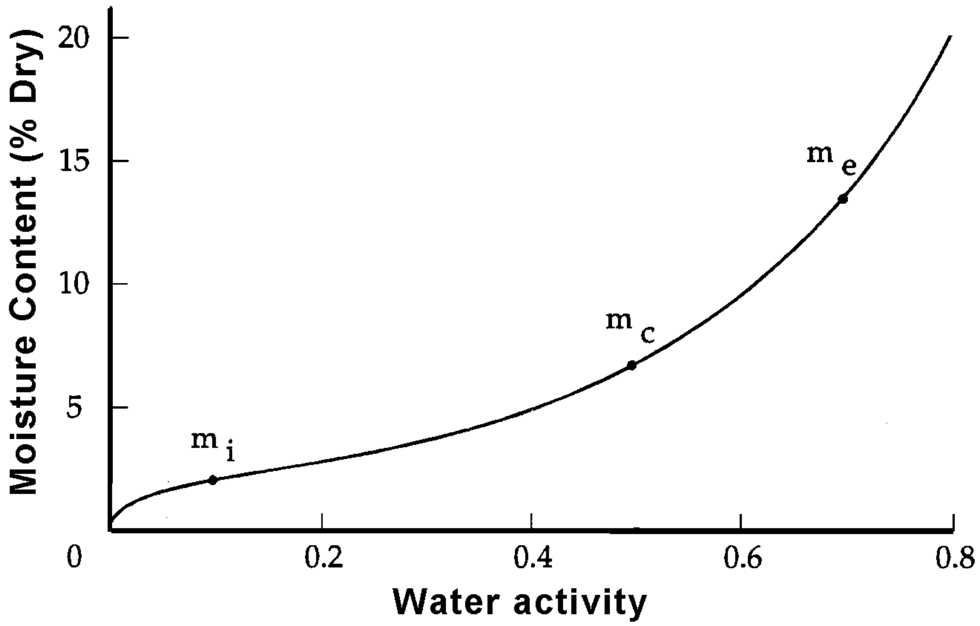

Figure 1. Typical moisture sorption isotherm (2).

FOOD AND BEVERAGE PRODUCTS	Oxygen gain, G (mg O_2/g of product)
Beer	0.001 – 0.004
Wine	0.003
Fruit Juice	0.02
Soda beverages	0.04
Coffee	0.11
Cheese	0.42
Milk and other products like:	0.015

Sauces, meat, vegetables and dry nuts	

Table 1: Allowed oxygen gain for some food and beverage products

Water vapor permeability			
STRUCTURE	Measured Permeability (g/m^2*day*atm)	Calculated Permeability (g/m^2*day*atm)	Variation (%)
PET (12 µm)/PP (38 µm)	18.11	17.32	4
PET (12 µm)/PP WHITE (38 µm)	19.38	20.90	-8
PET (12 µm)/PP (33 µm)	22.09	19.86	10
BOPP (25 µm)/BOPP(25µm)	7.76	7.45	4
BOPP (20 µm)/BOPP (20 µm)	10.41	10.77	-4
BOPP (17.5 µm)/BOPP MET. (17.5 µm)	1.04	1.04	-0.04

Table 2: Water vapor permeability for several film structures: Comparison between measured and model calculated data

Oxygen Permeability. Low barrier films			
STRUCTURE	Measured Permeability (ml/m^2*day*atm)	Calculated Permeability (ml/m^2*day*atm)	Variation (%)
BOPP (20µm)/BOPP PEARL (30µm)	715.890	959.080	-34
BOPP (20 µm)/BOPP (20µm)	774.960	956.910	23
BOPP (25µm)/BOPP(25µm)	783.070	579.960	26

Table 3: Oxygen permeability for several low barrier films: Comparison between measured and model calculated data

Oxygen Permeability. Medium barrier films			
STRUCTURE	Measured Permeability (ml/m^2*day*atm)	Calculated Permeability (ml/m^2*day*atm)	Variation (%)
PET (12 µm)/BOPP PEARL (30 µm)	96.950	90.520	7
PET (12 µm)/PP (38 µm)	113.520	90.120	21
PET (12 µm)/PP WHITE (38 µm)	113.190	90.124	20
PET (12µm)/PP WHITE (51 µm)	96.340	88.560	8
PET (12 µm)/PP (33µm)	109.920	90.730	17

Table 4: Oxygen permeability for several medium barrier films: Comparison between measured and model calculated data

Oxygen Permeability. High barrier films			
STRUCTURE	Measured Permeability (ml/m^2*day*atm)	Calculated Permeability (ml/m^2*day*atm)	Variation (%)
PA (46 µm)/EVOH-F (8 µm)/PP (28 µm)/PE-m (25 µm)	0.845	0.812	3.83
PP (18 µm)/EVOH F (4 µm)/PP (18 µm)	1.671	1.687	-0.93
PE (21 µm)/EVOH L (4 µm)/PE (16 µm)	0.873	0.857	1.80

Table 5: Oxygen permeability for several high barrier films: Comparison between measured and model calculated data