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Predicting the headspace oxygen level due to oxygen permeation across multilayer polymer packaging materials: A practical software simulation tool

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ABSTRACT

The shelf life of a food product is largely determined by its chemical and microbiological stability. In this respect, the gas composition surrounding a packaged product plays a major role. Modified Atmosphere Packaging (MAP) is a packaging technique that usually reduces the headspace oxygen to a preferable minimum for most food products. Besides the residual oxygen, the O_2-permeability of the packaging material is also important, as it determines the amount of oxygen permeating into the package during storage. This paper describes the development of a practical software simulation tool to predict the amount of oxygen permeating into the headspace during storage for a variety of multilayer packaging configurations. The simulation tool gives access to simulation models for mono- and multilayer films, trays covered with top foils and bottles with caps. The user can compose his/her own (multilayer) packaging material and check the oxygen ingress over time for different temperature conditions for all packaging configurations.

Industrial relevance: The software simulation tool is of industrial relevance to food companies, as they can use it to select or compare different films, but also to underpin their choice for a certain packaging material with regard to the sensitivity of the food product to oxygen and the desirable shelf life. The simulation program also provides food companies with information about the influence of storage conditions, like time and temperature, on the ingress of oxygen in their food package throughout the storage-distribution chain. On the other hand, it can also be used by packaging suppliers to predict the oxygen permeability in the optimization process of new films and as a client support tool.

1. Introduction

Consumer demand for high quality, shelf stable and ready-to-eat food products has increased over the last decade. This has stimulated the rapid increase in the development of mildly preserved or preservative-free products that keep their natural and fresh appearance as far as possible (Guilbert, Gontard, & Gorris, 1996). As a result, more and more packaging films and techniques needed to be optimized to guarantee the safety of these products and to enhance their shelf-lives. Thus various packaging techniques have been developed considering the important role played by oxygen in various chemical (i.e. lipid oxidation, vitamin C degradation, etc.), microbiological (i.e. growth of spoilage and pathogenic micro-organisms) and physiological (i.e. browning, etc.) processes. One of the most important developments in this area is Modified Atmosphere Packaging (MAP). This gas packaging technique relies on a modification of the atmosphere surrounding the product, more specifically, a reduction of the oxygen concentration and an increase of the carbon dioxide concentration (Mahajan, Oliveira, Montanez, & Frias, 2007; Phillips, 1996; Smith, Daifas, El-Khoury, Koukoutsis, & El-Khoury, 2004). In most cases, the concentration of oxygen in a food package has to be kept as low as possible in order to reduce oxidative degradation and to preserve the quality of the product (Campanella, Antiochiaz, Dragonex, & Lavagniniz, 2005). The presence of oxygen not only leads to an increase in the oxidation of fats and important nutrients like vitamin C, but it also results in the decomposition of proteins, discoloration, formation of harmful peroxides or aldehydes, etc. In addition the oxygen concentration may also influence microbiological growth and metabolism (Kerry, O'Grady, & Hogan, 2006; Hong & Krochta, 2006).

Besides reducing the residual headspace oxygen levels by means of techniques like MAP, protection of the packaged food product against oxygen, by preventing its ingress, is therefore by far one of the most important functions of the packaging material (Hong & Krochta, 2006). The success of any packaging technique as a means of extending the shelf life is thus largely dependent on its permeability

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characteristics (Smith et al., 2004). The permeability depends highly on factors such as temperature, relative humidity and the nature of the polymer i.e. its crystallinity, orientation, concentration of plasticizer, etc. (Hertlein, Singh, & Weisser, 1995; Robertson, 2006). Ideally the material should be a good barrier to both oxygen and water vapour; whilst its flexibility, mechanical strength and transparency remain optimal and its cost low (Lange, Stenroos, Johansson, & Malmström, 2001; Robertson, 2006). To obtain desirable (barrier) characteristics, a flexible film is mostly composed of multiple layers, each with a specific function — the most important functions being sealing, gas and moisture barrier functions.

Therefore the objective of the work reported in this paper was to predict and compare the amount of oxygen that permeates through various multilayer packaging configurations i.e. films (mono- and multilayers), trays with topfoils and bottles with caps by developing a validated simulation tool. A similar user-friendly software has already been described in literature by Mahajan et al. (2007) for the selection of a suitable packaging material guaranteeing the optimal equilibrium Modified Atmosphere Packaging or EMAP conditions for fresh-cut produce like fruits and vegetables. Contrary to this work, the modeling tool described here emphasizes more the packaging aspect as such, like the combining effect of different monolayer materials with different oxygen barrier properties and different thicknesses on the oxygen permeability of the composed multilayer structure. It can be used for individual films as well as for combined packaging systems like trays and topfoils and bottles and caps. It takes into account the influence of important factors such as the time–temperature profile, type of polymer and film layer composition, but also the film thickness and residual oxygen level at the start of storage. In contrast with the EMAP-modeling program, which is designed especially for fresh-cut products, the design of this simulation tool is more general and applicable to the packaging of all types of food products. Although the respiration aspect for certain vegetables is also incorporated in the software described here as a simulation option, the program does not include the consumption of oxygen by microbiological growth or oxidation mechanisms. In future the link between the residual oxygen concentrations and food quality deterioration due to these processes will be explored on a wide variety of food products, providing information on the oxygen sensitivity of food products. This will result in an integrated or complementary use of these data with the simulation program described above.

2. Methodology

The structure underlying the software simulation tool is based on the O_2-permeability of films (mono- and multilayers), trays with top foils and bottles with caps, and includes the influence of the time and temperature, volume of the headspace, residual oxygen concentration after packaging, type of polymer and film layer composition, thickness of the individual layers, etc.

It should be mentioned that certain parameters like the glass transition temperature (T_g), which determines the transient state of the packaging material, and the relative humidity (RH) are not included in the model. Focusing on the oxygen permeability, the influence of the relative humidity can be neglected, due to the encapsulation of RH-sensitive layers (e.g. EVOH) between structural layers with a low water vapour transmission rate (WVTR) like polyolefins, which are good water vapour barriers (Robertson, 2006; Massey, 2003). With regard to the T_g, when considering different monolayer packaging materials for different food applications, the T_g is not covered by the temperature range (−18–25 °C) in which most food products are being stored, implying that the same physical transient state can be regarded for these storage temperatures (Robertson, 2006).

The design of the simulation program is thus based on an extensive literature research and required the O_2-permeability coefficients of different packaging materials at different temperatures. Detailed technical files and samples of the films concerned were needed. Besides these data, the experimental determination of the oxygen transmission rate (OTR) for caps, bottles and films was also undertaken.

2.1. Model equations

Fig. 1 schematically shows the permeation of a gas or water vapour molecule through a polymer packaging material. The transfer of the molecules through the film occurs by a sorption–diffusion–desorption mechanism, driven by the difference in partial pressure across the film. Based on this scheme, the definition of the permeability coefficient P (ml O_2 μm/m^2 d atm) is presented in Eq. (1):

$$P = \frac{QL}{At(\Delta p)} \tag{1}$$

this equation takes into account Q (ml O_2), the amount of permeant diffusing through a polymer of surface A (m^2) over a period of time t (d), L (μm) the thickness of the film and indirectly the headspace volume and initial oxygen concentration in the package by Δp (atm), the difference in oxygen partial pressure between the inner and outer atmosphere (Robertson, 2006). The differential equation (based on Eq. (1)) to calculate the amount of oxygen permeating through the packaging material is given by Eq. (2):

$$\frac{dO_2}{dt} = \frac{P*A*L*(20.9-O_2)}{V} \tag{2}$$

with V (ml) the headspace volume and O_2 (%) the residual headspace oxygen concentration.

The effect of temperature on P is quantified by the Arrhenius equation, given in Eq. (3), which was implemented in the simulation tool as Eq. (4):

$$P = P_0 \exp\left(\frac{-E_p}{RT}\right) \tag{3}$$

$$P = P_{ref} \exp\left[\frac{E_p}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \tag{4}$$

where P is the permeability of the polymer material at a certain temperature T (K), R is the ideal gas constant, P_0 a pre-exponential factor, E_p (kJ/mol) the activation energy of the permeability process, and P_{ref} (ml O_2 μm/m^2 d atm) and T_{ref} (K) are, respectively, the reference permeability coefficient and temperature. Eq. (4) enables

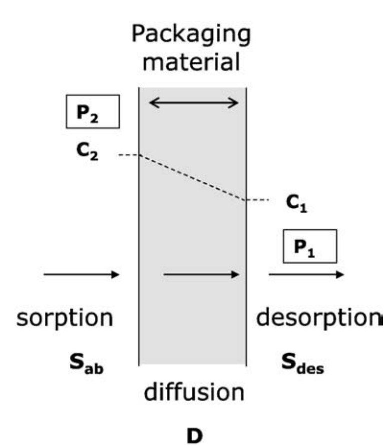

Fig. 1. Permeability model for gas and water vapour transport throughout a polymer packaging material (adapted from: Robertson, 2006) S_{ab} and S_{des}: absorption and desorption coefficient of the penetrating component, D: diffusion coefficient of the permeating component, P_1 and P_2: partial pressure of the permeating component at the respectively the inner and outer side of the packaging material, c_1 and c_2: concentration of the component at each side of the packaging material.

the calculation of permeability coefficients at temperatures (T) different from T_{ref} (Soney & Sabu, 2001; Robertson, 2006). The reference permeability coefficient and temperature in the program correspond to the permeability given in the technical file of a material and the temperature of the corresponding test condition, respectively. The software developed incorporates E_p-values found in literature for the most widely used packaging materials, which are listed in Table 1. Due to the limited number of values found in literature, a general E_p-value is often used in the simulation tool for a given type of polymer packaging material.

As mentioned earlier, to obtain a film capable of prolonging the shelf life of the product, most of the films used for food packaging are composed of different layers, each with a specific function. For the calculation of the permeability of a multilayer structure with n layers, Eq. (5) has been used:

$$P_T = \frac{L_T}{\frac{L_1}{P_1} + \frac{L_2}{P_2} + \ldots + \frac{L_n}{P_n}} \tag{5}$$

here the thickness of the total structure is L_T (µm), whilst $L_1, L_2, \ldots, L_n$ (µm) are the individual thicknesses of the corresponding layers. P_1, P_2, …, P_n (ml O_2 µm/m^2 d atm) stand for the corresponding permeability coefficients of the individual layers (Robertson, 2006; Solovyov & Goldman, 2004). In this formula only the constitutive layers are taken into consideration, while the possible influence of adhesives is excluded.

Besides the oxygen that enters the package, it is also foreseen that the software tool will have an option taking into account the oxygen that is consumed. This consumption would be either by respiration of fresh-cut vegetables or by oxygen scavengers.

To predict the consumption of oxygen by fresh-cut vegetables, the model designed by Jacxsens, Devlieghere, and Debevere (2000) was used. This model describes the oxygen and temperature dependence (in the absence of CO_2) of the respiration rate RO_2 (ml/kg d) for different types of fresh-cut vegetables using equations Eqs. (6) and (7).

$$RO_2 = \frac{V_{max} * (O_2)}{K_m + (O_2)} \tag{6}$$

where V_{max} is the maximum respiration rate (ml O_2/[kg*d]) and K_m is the Michaelis–Menten constant (ml/100 ml). The maximum respiration rate (V_{max}) increases exponentially with the temperature:

$$V_{max} = V_1 \exp(V_2 * T) \tag{7}$$

where V_1 is the pre-exponential factor (ml O_2/[kg*d]) and V_2 is a factor describing the temperature inverse. This exponential relation has been well established and has been determined for 10 fresh-cut products (Jacxsens et al., 2000). The coefficients V_1 and V_2 for these fresh-cut vegetables are shown in Table 2.

To predict the evolution of the O_2-level in the headspace when oxygen scavengers are used, the software has an option to consider active packaging material. When an oxygen scavenger is placed in the package, the absorption kinetics has to be taken into account. Only a few data and studies exist in literature concerning these kinetic parameters. Tewari et al. (2002) investigated six commercial oxygen scavengers and reported a first order absorption kinetic for all of them at both high and low initial oxygen concentrations. The consumption of oxygen by O_2-scavengers and the remaining concentration in the headspace is given by Eq. (8):

$$\ln(O_2) = -k * t + \ln(O_2)_{init} \tag{8}$$

in this equation, k (h^{-1}) is the absorption rate constant and $(O_2)_{init}$ the initial oxygen concentration (%). An overview of the Arrhenius equations relating the k-values for different commercial oxygen scavengers with the temperature are given in Table 3. The atmospheric condition 'air' in Table 3 refers to high oxygen concentrations (20.9%), while 'N_2 + air' refers to initial oxygen concentrations of 0.05%. As this low concentration (0.05%) is already considered by many food companies to be equal to zero and the packaging limit for residual oxygen is often considered to be above 0.5%, only the k-values for the high oxygen levels of the scavenger materials are included in the simulation tool.

The equations mentioned above are valid for films, but they can also be used for trays consisting of one or multiple layers and for bottles. For the combination of a tray with a top film, or the combination of a bottle with a cap, the sum has been taken of the oxygen permeating through each part, taking into account the packaging configurations, the permeability coefficients of the films and the time–temperature profile.

2.2. Design variables

Table 4 summarizes the design variables accounted for the simulation of oxygen diffusion through polymer packaging materials. In the simulation tool the user has to select first the type of packaging configurations (film, tray with top foils, bottles and caps) and the

Table 1
General activation energy (E_p) for permeation.

Type of packaging material	E_p (kJ/mol)
LLDPE	37.2[a]
LDPE	42.7[a]
HDPE	35.1[a]
PP	45.3[a]
PS	16.4[a]
EVOH (32% ethylene)	65.23[b]
EVOH (48% ethylene)	62.18[b]
PA	43.5[a]
PET (amorphous)	37.7[a]

[a] Source: Müller (2003).
[b] Source: Massey (2003).

Table 2
Coefficients K_m, V_1 and V_2 (±95% confidence interval) of the Michaelis–Menten equation (Jacxsens et al., 2000).

Type of product	K_m (ml/100 ml O_2)	V_1 (ml O_2/(kg h))	V_2 (1/K)
Bell peppers (0.004 × 0.01 m)	0.77 ± 0.46	1.41E−12 ± 0.46E−12	0.11 ± 0.01
Brocoli florets	14.39 ± 2.3	4.27E−18 ± 1.43E−18	0.16 ± 0.01
Carrots (grated)	5.71 ± 1.37	1.22E−14 ± 0.50E−14	0.13 ± 0.01
Chicory endives (0.005 m)	5.97 ± 0.85	1.48E−23 ± 0.64E−23	0.19 ± 0.02
Chicory endives (heads)	7.11 ± 0.41	5.75E−19 ± 2.68E−19	0.16 ± 0.02
Cucumber (0.003 m)	3.71 ± 0.38	1.34E−14 ± 0.55E−14	0.12 ± 0.01
French beans (0.01 m)	9.17 ± 2.45	6.11E−26 ± 3.69E−26	0.22 ± 0.02
Iceberg lettuce (0.01 m)	5.72 ± 2.08	1.35E−14 ± 0.60E−14	0.12 ± 0.01
Mixed lettuce	9.92 ± 0.67	2.55E−11 ± 0.57E−11	0.09 ± 0.01
Mungbean sprouts	0.45 ± 0.16	3.54E−23 ± 1.16E−23	0.19 ± 0.01

Table 3
Arrhenius equations for different oxygen scavengers (Tewari et al., 2002).

Scavenger-type	Atmosphere	Arrhenius equation for the absorption rate constant k[a]
Ageless® FX-100	Air	$k = 484077.4 \exp^{(-6004.03/T)}$
	N_2 + air	$k = 0.005 \exp^{(-1118.23/T)}$
Bioka® S-100	Air	$k = 13082.1 \exp^{(-5379.43/T)}$
	N_2 + air	$k = 2.04 \exp^{(-3169.74/T)}$
FreshPax® M-100	Air	$k = 1636 \exp^{(-5301.5/T)}$
	N_2 + air	$k = 7404511.2 \exp^{(-7703.6/T)}$
	CO_2 + air	$k = 1480.3 \exp^{(-5129.87/T)}$
freshPax ® R-300	Air	$k = 0.006 \exp^{(-881.25/T)}$
	N_2 + air	$k = 0.41 \exp^{(-2487.72/T)}$

[a] k: rate constant (s^{-1}); T: absolute temperature (K).

Table 4
Design variables involved in the software package.

	Variables	Designation	Unit
Oxygen ingress			
Surrounding-related	Time-interval	t	d
	Temperature	T	°C
Product atmosphere-related	Volume product	V_{prod}	ml
	Total volume packaging	V_{pack}	ml
	Initial oxygen concentration	$O_{2(init)}$	%
Packaging configuration	Permeability to oxygen at the given test conditions	P_{test}, P_{ref}	ml O_2 µm/m^2 d atm
	Test temperature	T_{test}, T_{ref}	°C
	Activation energy	E_p	kJ/mol
	Area of film available for gas exchange	A	m^2
	Thickness	L	µm
Oxygen consumption			
Respiration vegetables	Respiration rate and maximum respiration rate	RO_2, V_{max}	ml O_2/(kg d)
	Pre-exponential factor	V_1	ml O_2/(kg d)
	Factor describing inverse temperature	V_2	K^{-1}
	Michaelis–Menten constant	K_m	(ml/100 ml)
Oxygen absorber	Kinetic absorption rate constant	k	(d^{-1})

number of layers of a given film, tray, top foil, etc. Subsequently, access is given to the appropriate simulation model. Once an appropriate simulation model has been selected, the user has to define the variables needed for the simulation. The user can enter the time–temperature profile that has to be considered. It should be noted that the time–temperature profile is implemented as a step-function (as time–temperature combinations) to simulate a change in temperature during the transport or storage of a packaged food product. Because of this step-function the tool does not take into account the realistic gradual increase or decrease of the temperature in the product throughout the storage-distribution chain. Some variables are also linked, e.g. once a monolayer film (i.e. LDPE) is selected, the general E_p for this type of film is fixed as well.

3. Graphical user interface

The graphical user interface was built and compiled in Matlab Guide version R2006b (The Mathworks, Gouda, The Netherlands). The program provides a primary interface with tabs to access submenus called 'Packaging' and 'Manual'. The packaging menu has a link to access two built-in databases under the 'Databases' tab, while the 'Simulations' option menu lists the simulation possibilities for the different types of packaging configurations considered in this software tool. For films a second choice can be made for monolayer or multilayer films (see Fig. 2).

3.1. Packaging

3.1.1. Databases

A link to two Excel-based databases was incorporated in the tool to provide access to permeability coefficients of different types of polymer packaging materials at different temperatures. Hereby, one database covers data for monolayer films. This database provides

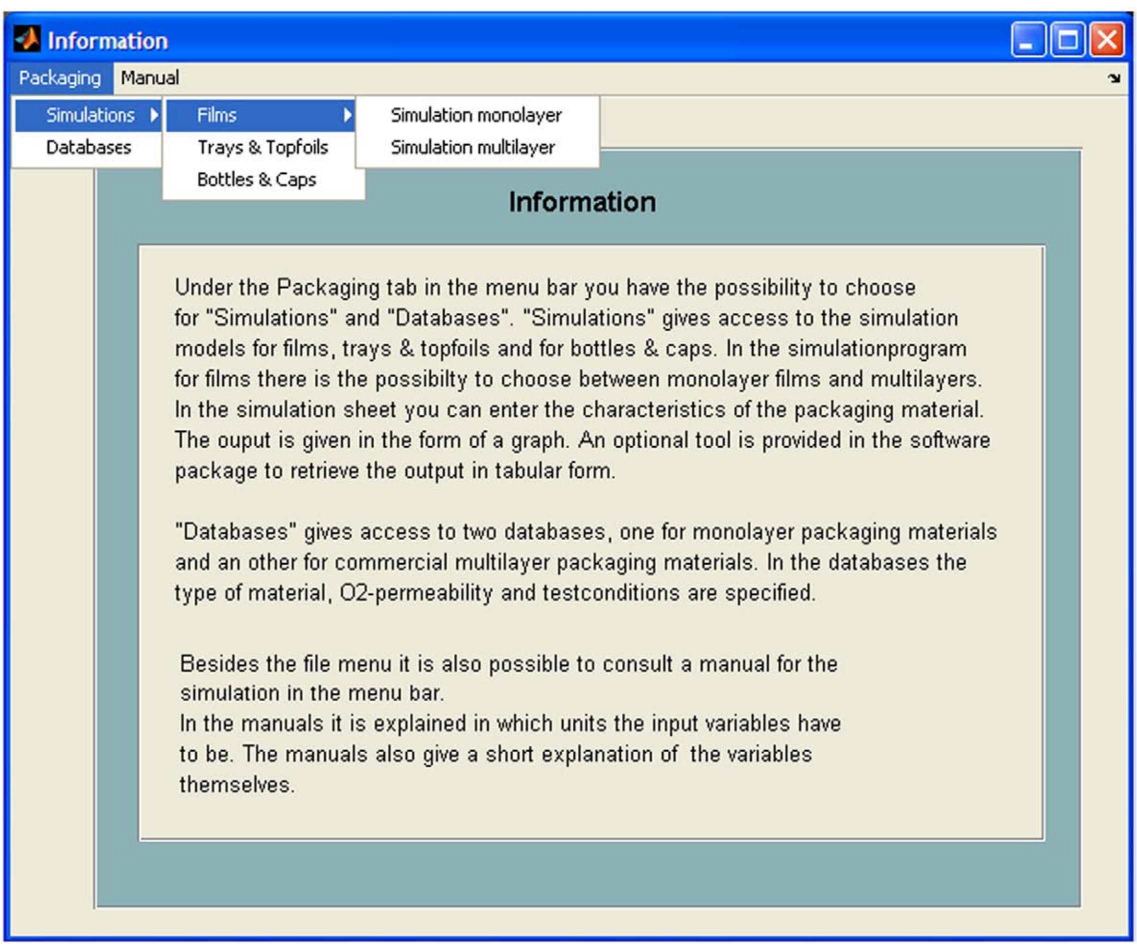

Fig. 2. Software window with main menu.

access to permeability coefficients and their corresponding test conditions for different types of monolayer materials, which can be filled in by the user to construct a certain multilayer polymer film for the simulation purpose. The second database is more informative and provides information about multilayer films and their corresponding structure and oxygen transmission rates (OTR, ml O_2/m^2 d atm). These databases were realised by collecting datasheets and technical files from food companies as well as from manufacturers of packaging materials and also by data found in literature.

By selecting the 'Databases' tab under the 'Packaging' option access to the built-in databases is given.

3.1.2. Simulations and selection of the packaging configuration

3.1.2.1. Films. As mentioned previously, when the simulation of films is requested, an additional choice can be made between a simulation for a monolayer or a multilayer film. For a multilayer film consisting of several layers, the user can compose films with 2, 3, 5 or 7 layers. Once the user has defined the temperature–time profile and the other single input variables specifying the packaging configurations (volume headspace, area, etc.), a tab can be used to access a window where a plot of the oxygen ingress over the time–temperature profile is shown. Fig. 3 shows an example of the input menu. An option is available to collect the results in an Excel file, thereby allowing the user to save the different simulations and compare the explicit values to one another. Furthermore, different simulations (different input conditions) can be compared by plotting the curves in a single graph. These options are also available for the other packaging combinations.

3.1.2.2. Trays and top foils. As for the options discussed above for films, the different combinations for mono- as well as for multilayers can be made for each part of the packaging combination that constitutes the tray and foil package. Figs. 4 and 5 show the interface for selecting the packaging combination of trays and top foils respectively. For trays (but also for bottles and caps (see next paragraph)), the remark should be made that the simulation tool does not take into account possible thinner, weaker sides or corners of the tray, which could be formed due to the stretching during thermo-formation. The simulation tool assumes thus an equal thickness on the overall tray surface and can result in a possible underestimation of the residual oxygen concentration.

3.1.2.3. Bottles and caps. After defining the permeability for both the bottle and the cap, and after specifying the bottle volume and initial oxygen concentration, the simulation can run for this type of packaging combination over the chosen time–temperature profile.

3.2. Manual

The manual provides the user with information about the different options and the various possibilities of the software. It also points out various practical aspects including the units of the various variables and other aspects.

4. Validation

Validation was performed for monolayer and multilayer films and for the combination of bottles and caps, hereby taking into account different temperature conditions.

4.1. Materials and methods

4.1.1. Films

For the monolayer films, glass jars ($n = 3$) were covered with a foil (Agrifresh 50 EA; oxygen transmission rate = 3600 ml O_2/m^2 d atm (23 °C, 0% relative humidity); Amcor Flexibles, Herfordshire, UK) and sealed to prevent oxygen passing through the closure. Before sealing

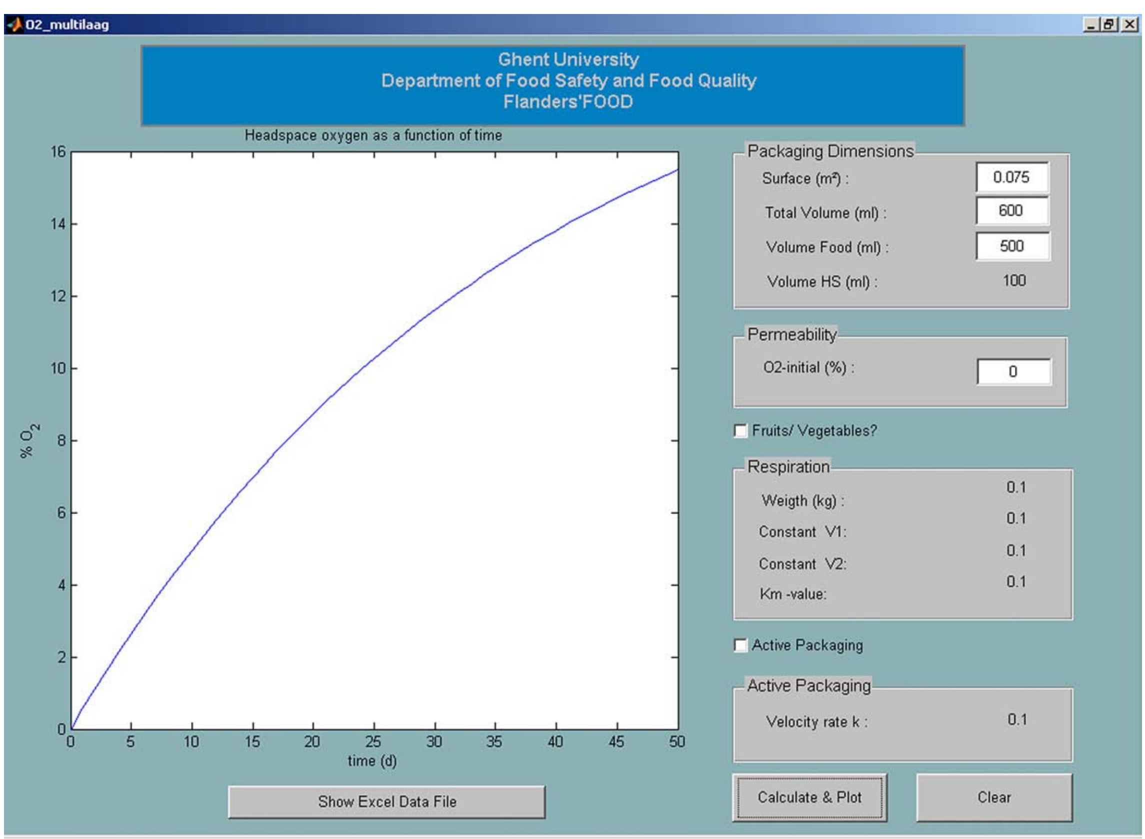

Fig. 3. Software window after clicking on the "simulation" tab, reflecting the variables which have to be given in by the user.

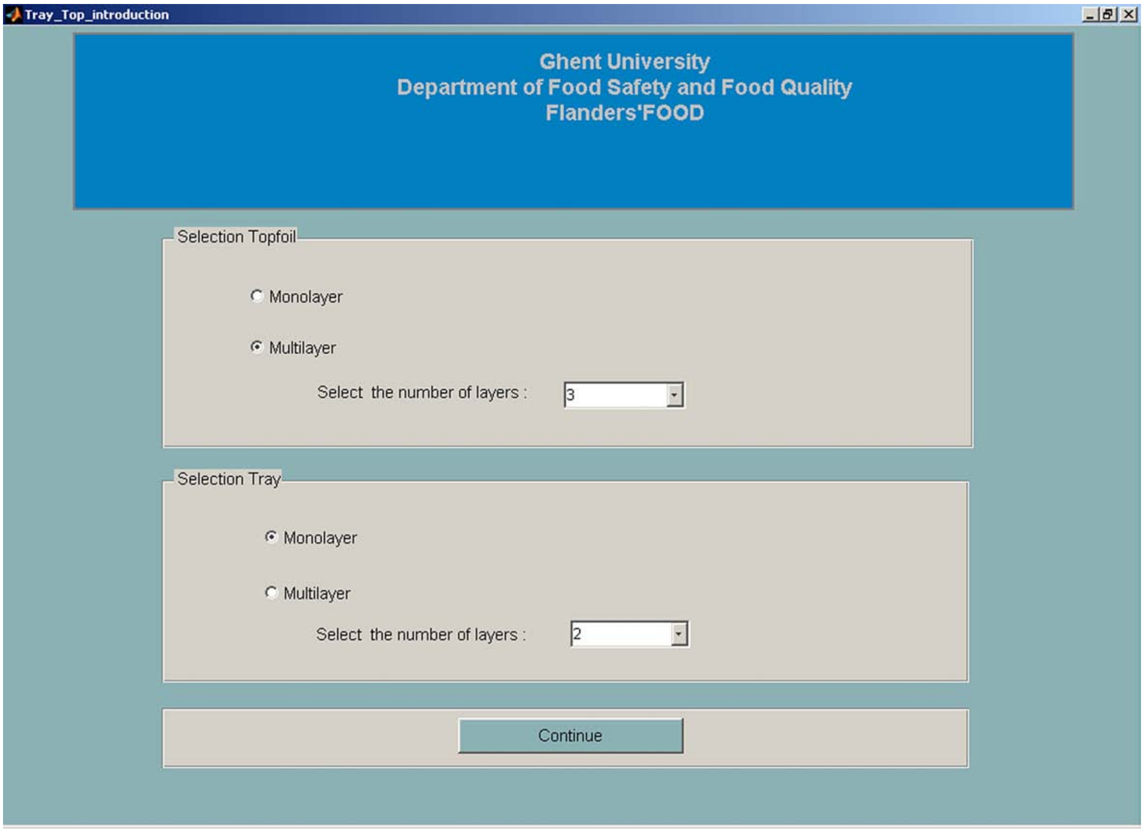

Fig. 4. Software window showing the combination interface for the packaging combination of a tray and top foil.

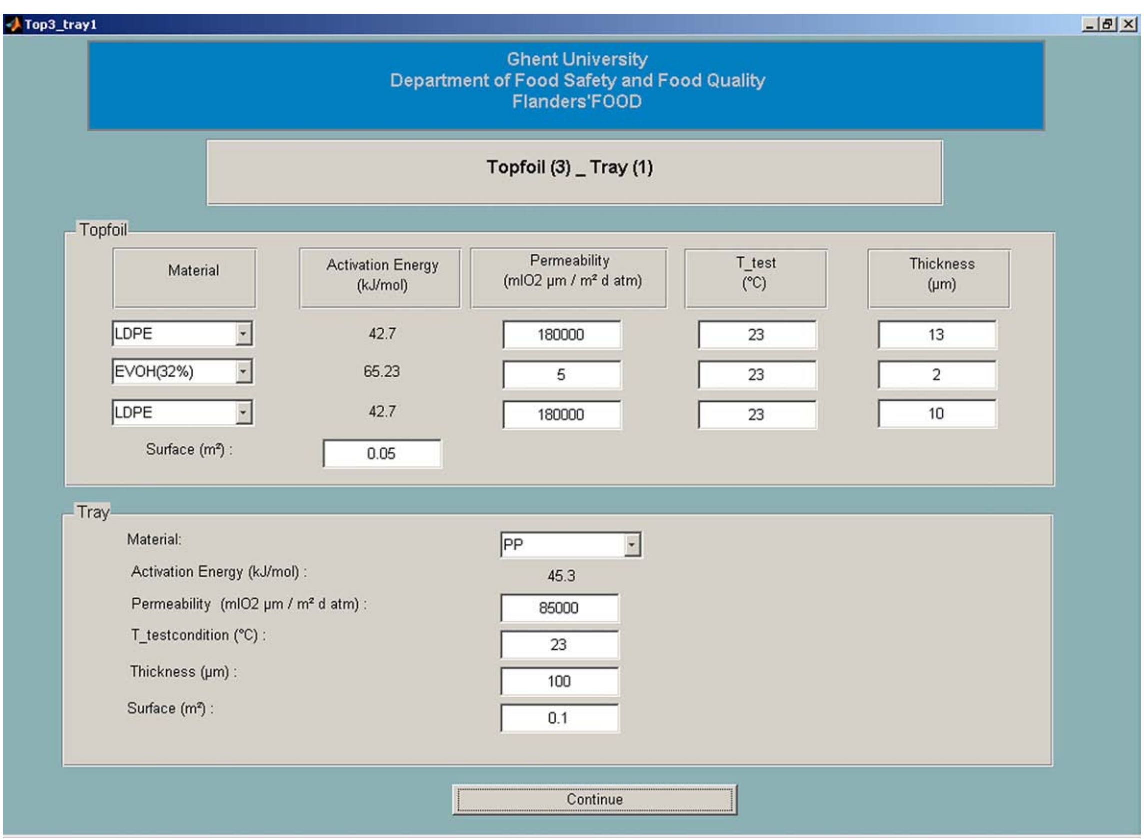

Fig. 5. Software window after selection of the combination for a 3-layered top foil (LDPE/EVOH/LDPE) and a tray consisting out of one polymer packaging material (PP).

and storage at 7 °C, the jars were flushed with 100% of N_2 (Freshline, Air Products, Brussels, Belgium) and an Oxydot (ETS, Kieldrecht, Belgium) was sticked to the jar wall. At regular time intervals, the oxygen concentration in the headspace was measured non-invasively with an OxySense®T210 (ETS, Kieldrecht, Belgium). The observed values were compared to those obtained by the simulation program for the same conditions.

For the validation of the multilayer film (PE/PA, OTR = 30 cm³/m² d (26 °C, 90% RH), Enplater S.A., Girona, Spain), the simulation results for the total film at 30 °C, obtained using the technical data for each composite layer (*P* at 26 °C), were compared to the results from a permeability test (Mocon Oxtran 2/21, Mocon®, Minneapolis, Minnesota, USA) for the whole film at a different temperature (OTR at 30 °C). In addition to this theoretical comparison, an experimental validation for this film was also carried out at 30 °C in the same manner as described for the monolayer films ($n = 2$).

4.1.2. Bottles and caps

For the combination of bottles and caps, 3 PET-bottles (500 ml; OTR = 0.17 cc/[pkg d] at 22 °C, 50% RH) were closed by hand with polypropylene caps (OTR = 0.0611 cc/[pkg d] at 22 °C, 50% RH). An Oxydot was placed in each bottle before closure, after which they were flushed with pure N_2 and stored at 22 °C. For validation, the actual permeabilities of the bottles and caps at 22 °C were tested separately using the Mocon Oxtran 2/21. These values were entered in the software simulation tool to predict the evolution of the headspace O_2-concentration. The measured evolution of headspace O_2 was then compared to that predicted using the tool.

4.2. Statistical analysis

To objectively evaluate the performance of the simulation tool, comparisons between the observed and predicted O_2-concentrations were made using the following indices: the determination coefficient R^2, bias factor (B_f) and accuracy factor (A_f) (Baranyi, Pin, & Ross, 1999; Pin, Sutherland, & Baranyi, 1999). For graphical validation, plots of predicted versus observed O_2 were also constructed to visually assess for bias and general interpolation abilities.

Table 5
Statistical parameters of the simulation tool validation.

	Monolayer ($n = 3$)	Multilayer ($n = 2$)	Bottle and cap ($n = 2$)
R^2	99.84	99.34	86.82
B_f	0.9437	0.7883	1.0319
A_f	1.0715	1.507	1.0906

4.3. Results

Fig. 6(a) represents the experimental and simulation data for the monolayer at 7 °C. An R^2-value of 99.8% was obtained, indicating a good fit. The overall discrepancy or error (7.15%) between the model and the observations is smaller than 10%, confirming this assessment. The bias factor (B_f) on the other hand shows a small underestimation (0.9437) by the simulation, also visible in Fig. 6(b), showing the predicted versus the observed values. Table 5 gives an overview of all statistical parameters used to evaluate the performance of the tool.

In the first instance, for the validation of the multilayer film, a theoretical comparison was performed by, comparing the simulation data for the composed multilayer structure at 30 °C — starting from the permeability data of the individual layers at 26 °C — with data calculated for a shelf life of 350 days from the experimentally determined oxygen transmission rate at 30 °C. Both curves coincided and gave an R^2-value of 99.9%.

As for the experimental validation part, similar graphs as for the validation of the monolayer film are obtained for the multilayer film stored at 30 °C (Fig. 7(a) and (b)). According to the statistical parameters, this fit has an R^2-value of 99.3%, indicating a good fit. Nevertheless, the % *D* shows an average relative deviation of 50% and a B_f of 0.7883 showing an underestimation for the majority of the data points. In comparison with monolayer films, it is a logical consequence that the theoretical composition of several individual layers to one

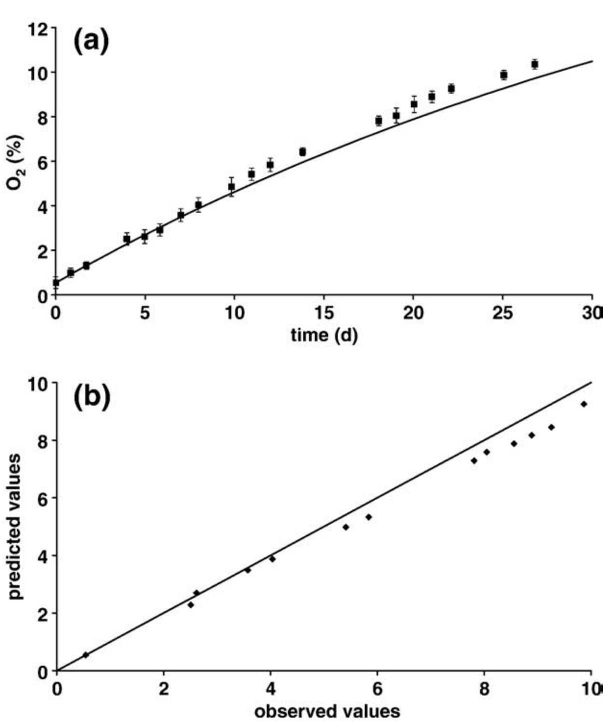

Fig. 6. (a). Oxygen ingress through a monolayer film (50 EA, 7 °C). (b). Predicted versus observed values for the monolayer EA film.

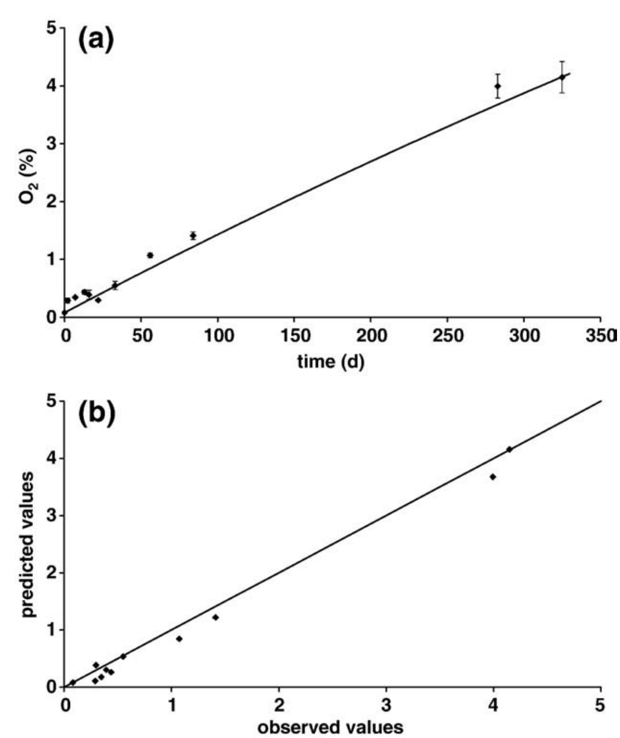

Fig. 7. (a). Oxygen ingress through a PE/PA multilayer film (Entplater, 30 °C). (b). Predicted versus observed values for the PE/PA multilayer film.

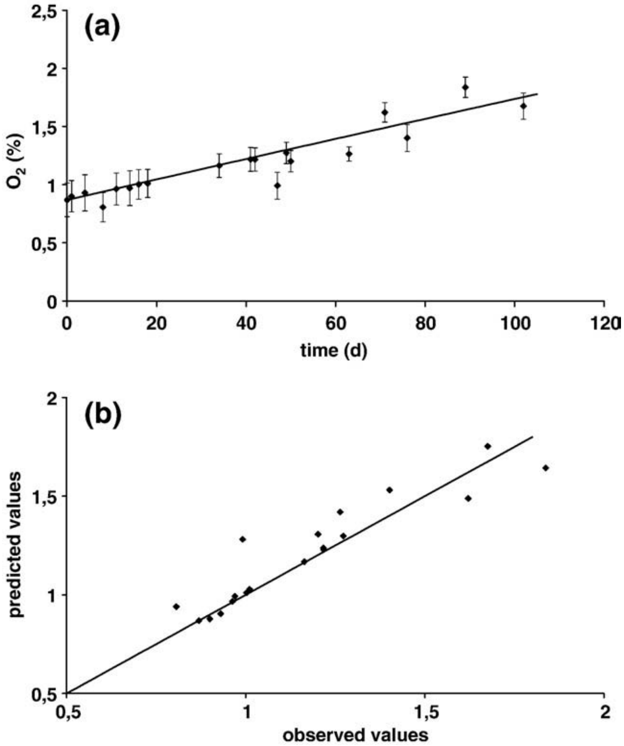

Fig. 8. (a). Oxygen ingress through a combination of a PET-bottle and PP-cap. (b). Predicted versus observed values for the combination of a bottle and cap.

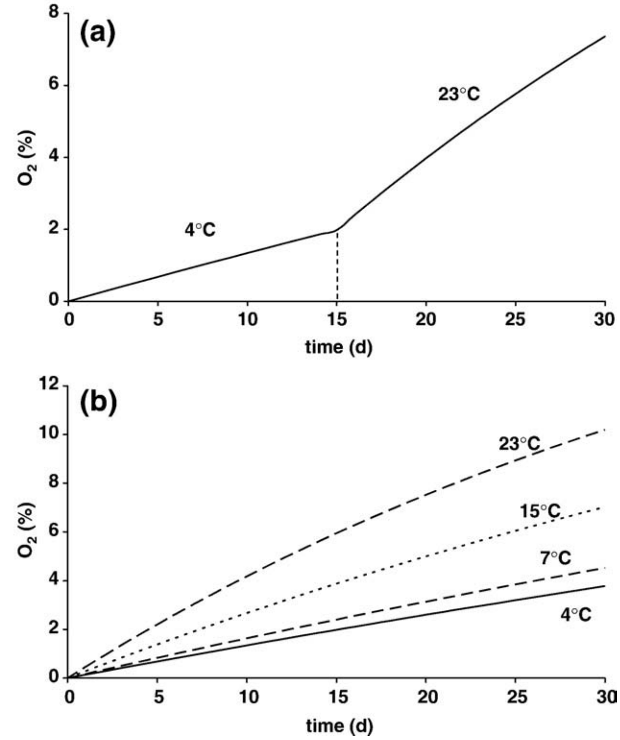

Fig. 9. (a). Influence of the time–temperature storage conditions on the oxygen permeability of a PE/PA-film. (b). Temperature effect on the O_2-permeability of a PE/PA-film.

monolayer structure implies a larger deviation from the experimental values of the actual film. Not only the variability of E_p for each layer, but also the variability in the individual permeability and thickness can increase the overall deviation. In addition, other factors can have an influence such as the non-uniformity of the thickness of the layers and the use of adhesives, which are not taken into account in the simulation tool.

In the case of 'bottle and caps' a good fit ($R^2 = 0.86$) can be seen in Fig. 8(a) and (b). Contrary to the previous simulations, the bias factor here is larger than 1 (1.0319), indicating a small overestimation (3%), while the percent deviation amounts to 9%.

5. Case study

Two case studies are presented to illustrate the usefulness and possibilities of the simulation tool. In the first case study the storage-temperature influence is elucidated, while in the second case the influence of the thickness, type of packaging material and headspace volume is discussed.

5.1. Influence of storage-temperature

Temperature is one of the most important factors influencing the permeability of a polymer packaging material. The permeability increases with increasing temperature according to the Arrhenius equation Eq. (3). Fig. 9(a) reflects the influence of the temperature on the oxygen concentration in the headspace (gas/product = 1/5) of a product packed in a PE/PA-film (OTR = 30 ml/m^{2}d atm, 26 °C, 0% RH) over a 30 day period when the temperature increases on day 15 from 4 to 23 °C. Fig. 9(b) shows the influence of several storage temperatures over the same storage period. Both figures clearly show an increase of oxygen ingress with increased storage temperature. After 20 days of storage at 4 °C a headspace oxygen concentration of 2.6% is obtained, while storage at 7 °C results in 3.1% of O_2 in the headspace. A temperature of 15 °C on the other hand raises the oxygen concentration to 5% after the same storage period.

5.2. Influence of the packaging configuration

According to the definition of permeability Eq. (1) incorporated in the simulation tool, an increase of the film thickness or the headspace volume will result in a decrease of the oxygen headspace concentration. EVOH is commonly known and used as oxygen barrier encased in between two polyolefin layers. However, different types of EVOH are on the market and applied in different thicknesses in the concerning packaging materials. Simulations at 23 °C with an EVOH layer of 32% (P = 5.13 ml µm/m^2 d atm; 23 °C; 0% RH) and 42% ethylene (P = 45.85 ml µm/m^2 d atm; 23 °C; 0% RH) of 2 µm in a PE/EVOH/PE film demonstrates the effect of the type of EVOH (Fig. 10). As confirmed by literature (Massey, 2003), the permeability of EVOH increases with increasing ethylene concentration. As can be seen in Fig. 10, an increase of this barrier thickness from 2 to 4 µm, while

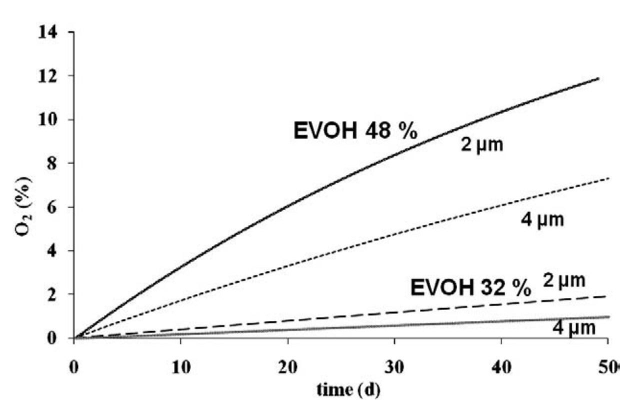

Fig. 10. Influence of thickness and type of packaging material on the O_2-permeability.

keeping the other conditions and packaging configurations constant, doubles the period required to reach a headspace oxygen concentration of 5%.

6. Conclusions

A practical, user-friendly software simulation tool has been developed to predict the headspace oxygen concentration in different packaging configurations and storage conditions. The software enables the user to check or compose a new film or packaging combination and visualize the oxygen ingress over time for different time–temperature profiles. Simulations can be performed to check the influence of different types of packaging materials, the effect of the thickness, temperature and headspace or product volumes on the oxygen concentration. By means of a validation with independently collected data, the reliability of the software package has been demonstrated.

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