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Evaluation and Modeling of Scavenging Performances of Active Multilayer PET Based Films for Food Preservation

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This work deals with the design, production and evaluation of the effectiveness of multilayer active systems based on PET, suitable for food packaging applications. Symmetrical 3-layer structures were produced by using a cast co-extruder laboratory-scale equipment. The oxygen scavenger (OS), copolyester based and approved for direct food contact, was added to the central layer. Two multilayer active films were obtained by keeping constant the thickness of the active layer and with different thicknesses of the inert layers. Active single layer and neat films were also produced for comparison. Oxygen absorption measurements in continuous were performed by means of a luminescence lifetime detection device. The scavenging performances, in terms of scavenging activity, exhaustion time and residual oxygen concentration in the package were investigated; in particular, their variation as function of the thickness variation of the inert layers was analysed. Preliminary shelf life tests were also conduced on *Brassica oleracea* florets, in order to point out the effectiveness of the OS systems in inhibiting vegetables senescence. Finally, a mathematical model, developed during previous studies, was applied to the data set in order to validate it and verify its effectiveness in predicting the transport phenomena occurring in the multilayer active systems.

Keywords: Oxygen scavenging, Mathematical modelling, Polyesters, Food packaging, Active films

1. Introduction

Active packaging solutions, by using Oxygen Scavenger (OS) systems, represent an innovative strategy to absorb the residual oxygen after packaging, ensuring freshness and safety through the time and minimizing quality changes of O_2-sensitive foods (Cruz et al., 2012). OS integration into polymer matrices, in order to produce active packages by means of conventional processes, represents a technological solution able to overcome addition of visible bags or cards, which could be not accepted by the consumer (Galdi et al., 2008). Physical and chemical phenomena involved during oxygen scavenging process in polymers were previously discussed (Di Maio et al., 2015).The main issues related to the application of this technology to flexible packaging concern storage and handling difficulties, as well as the necessity to prolong the OS effectiveness during the time, avoiding its premature and excessively fast oxidation. A possible solution is represented by the realization of multilayer structures, by inserting the active layer between two or more inert, barrier layers, with the aim of reducing the permeability to external gases and control the diffusive flux of the oxygen towards the central layer. Joining the active and the passive barrier, combined in a multilayer structure, creates a synergistic system with a dual oxygen fighting role: the oxygen scavenger into the central layer traps and reacts with molecular oxygen, whereas the outer layers improve the passive barrier, controlling the rate at which the OS exhausts.

The main goal in the selection of the OS and the design of the most appropriate active multilayer system becomes adapting the performances of the package to the requirements of the specific food product, in terms of respiration rates, sensitivity to environmental parameters and shelf life parameters. Clearly, there are many variables to consider, with a very large experimental matrix to explore. Mathematical modelling could represent a useful tool to describe the transport phenomena occurring in the multilayer active films, allowing knowing in advance which are the optimal parameters to achieve the best packaging performances, in terms of barrier and scavenging properties.

In this work, symmetrical, active multilayer structures were developed in order to control the exhaustion kinetic of the OS, through the control of the diffusion kinetic of oxygen through the layers. All the layers were made of Polyethylene Terephthalate, thus minimizing environmental impact and recyclability issues of the packaging. PET was also selected in virtue of its oxygen barrier properties, if compared with other polymers commonly used for packaging applications (Lange and Wyser, 2003).

A mathematical model, developed during previous studies (Bedane et al., 2015) was applied in order to investigate, at mathematical level, oxygen diffusion and sorption phenomena through the layers, as well as the exhaustion kinetics of the scavenger occurring into the active layer.

2. Experimental

2.1 Materials

The selected matrix is PET resin Cleartuf P60 (M&G Polimeri S.p.A., Patrica (FR), Italy), having intrinsic viscosity 0.58 dL/g. The active phase is a new generation of polymeric oxygen scavenger, named Amosorb DFC 4020E (AMS, supplied by Colormatrix Europe, Liverpool, UK). This is a copolyester-based polymer designed for rigid PET containers, characterized by an auto-activated scavenging mechanism. Both PET and AMS comply fully with FDA and EU food contact legislation.

2.2 Preparation of the active systems

The PET was dried under vacuum at 130 °C for 16 h, before processing. The AMS, delivered dried in aluminum bags sealed under vacuum, was used as received. The multilayer active films were produced by using a laboratory co-extrusion cast film line (Collin, Teach-line E20T), equipped with three single screw extruders (D=20, L/D=25), a flow convergence system (feed-block), a coat-hanger type head (slit die of 200 x 0.25 mm2) and a take-up/cooling system (chill rolls) thermally controlled by water circulation at 50 °C. The chill roll speed was 7 m/min, thus allowing the films to be stretched to their final dimensions of about 170 mm wide. Two symmetrical “ABA” three layer structures were produced, by locating the active layer (containing PET + 10 wt % AMS) between two skin layers of pure PET. The percentage of the oxygen scavenger added to the central layer (10 wt %) was already optimized by previous published studies (Galdi and Incarnato, 2011). The temperature profile for the two extruders was set to 280 °C from the hopper to the die. The thickness of the active layer was kept constant during processing, whereas the thickness of the inert layers was increased from 6.75 μm to 11.75 μm. Total and each layer thicknesses for coextruded films produced is reported in Table 1. Single layer films made of neat PET and active PET (i.e., PET loaded with 10 wt % of AMS) were also produced, for comparison, using the same apparatus and processing conditions.

2.3 Characterization methods of the produced films

Oxygen absorption measurements were carried out at 25 °C in continuous mode by means of the fiber optical oxygen meters Minisensor Oxygen Fibox 3-Trace V3 and Stand-alone Oxygen Meter Fibox 4 (PreSens GmbH, Regensburg, Germany), equipped with a polymer optical fiber and oxygen sensor spots SP-PSt3-NAU (detection limit 15 ppb, 0–100 % oxygen). Experiments were conducted on cut film samples with a defined geometry (8 x 4.5 cm^2), which were introduced in glass measurement cells, having volume equal to 9 ml, and hermetically capped. Then, oxygen consumption inside the closed glass vial was measured during the time.

The effectiveness of the active films in preserving the quality of fresh vegetables was preliminary verified by analysing the yellowing over the time of untreated, fresh-cut broccoli florets (*Brassica oleracea L. var. Italica*). Broccoli were cut in florets by using knives, mixed thoroughly in order to ensure a random selection and precooled overnight prior to packaging. Then, florets of uniform size and visual appearance and free of defects were divided into single bags, each one measuring 15 x 10 cm^2 in size, and approximatively of the same weight, completely sealed and then stored in a refrigerator at 5 °C for 15 days. The colour of fresh-cut broccoli florets was measured on homogeneous spot areas of 4 mm in diameter, by means of a colorimeter Minolta CR-300 (Konica Minolta International, Japan). The measurements were taken on all the samples at day 0 and after 15 days of storage. Ten measurements were performed on each floret, in order to homogeneously cover the whole surface, and then an average value was calculated for each parameter.

Table 1: Total and single layer thicknesses for active films produced

Sample	Total thickness [μm]	Inert layer 1 [μm]	Active layer [μm]	Inert layer 2 [μm]
Active Mono	25	-	25	-
Active Multi A	37	6.75	23.5	6.75
Active Multi B	47	11.75	23.5	11.75

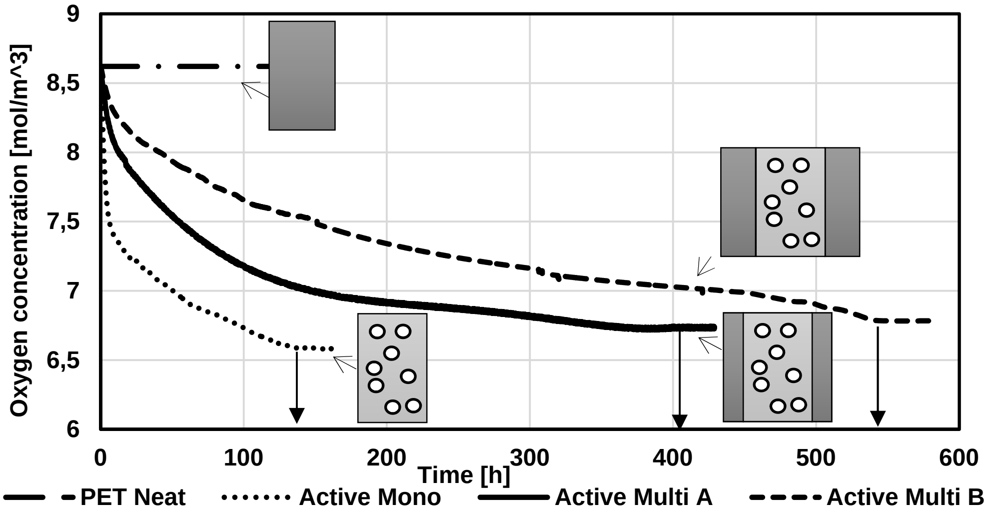

Figure 1: Oxygen absorption kinetics for PET Neat, Active Mono, Active Multi A and Active Multi B films

The colour variation of the same broccoli florets over time was evaluated by means of the colour-difference equation CIELAB ΔE^*_{ab}, based on the coordinates L*, a* e b* (CIE. Colorimetry, 1986).

2.4 Mathematical modelling

Mathematical description of the model, as well as its governing equations and parameters, was already provided during previous published studies (Bedane et al., 2015). Briefly, a symmetrical, multilayer polymeric film of total 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. A one dimensional transient diffusion in a medium bounded by a container (vial) filled with air, in which all diffusing material (O_2) 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. In addition, the scavenger and the products of its reaction with the permeant (O_2) are assumed to be immobile, thus there is no diffusion in the system other than solute diffusion. One-dimensional diffusion-reaction equations 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 used, considering the initial and boundary conditions specified earlier. In order to analyse 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.

3. Results and discussion

In order to investigate the oxygen scavenging performances of the multilayer active films, oxygen absorption analysis in continuous were performed. Figure 1 shows the oxygen absorption kinetics obtained for the 3-layer active samples, together with those of the single layer neat and active PET films. Oxygen absorption curves are expressed in terms of oxygen concentration [mol/m^3] against the time [h].

As expected, no gas consumption is observable for PET neat film, whereas for the active films the OS phase inside the polymer matrix immediately and irreversibly reacts with the oxygen, by trapping it, and a decrease in the oxygen concentration inside the vial is appreciable during the time, up to reach a plateau value. This behaviour points out the exhaustion of the scavenger, and the end of the scavenging activity. From continuous O_2 measurements it is also possible to calculate active film absorption properties: the exhaustion time t_{LE} (i.e the time for reaching the plateau stage, at which the O2 concentration becomes constant) and the scavenging

Table 2: Exhaustion time t_{LE} and Scavenging capacity μ for Active Mono, Multi A and Multi B films

Sample	t_{LE} [h]	μ [ccO_2/g]
Active Mono	120	4.68
Active Multi A	400	3.64
Active Multi B	550	2.47

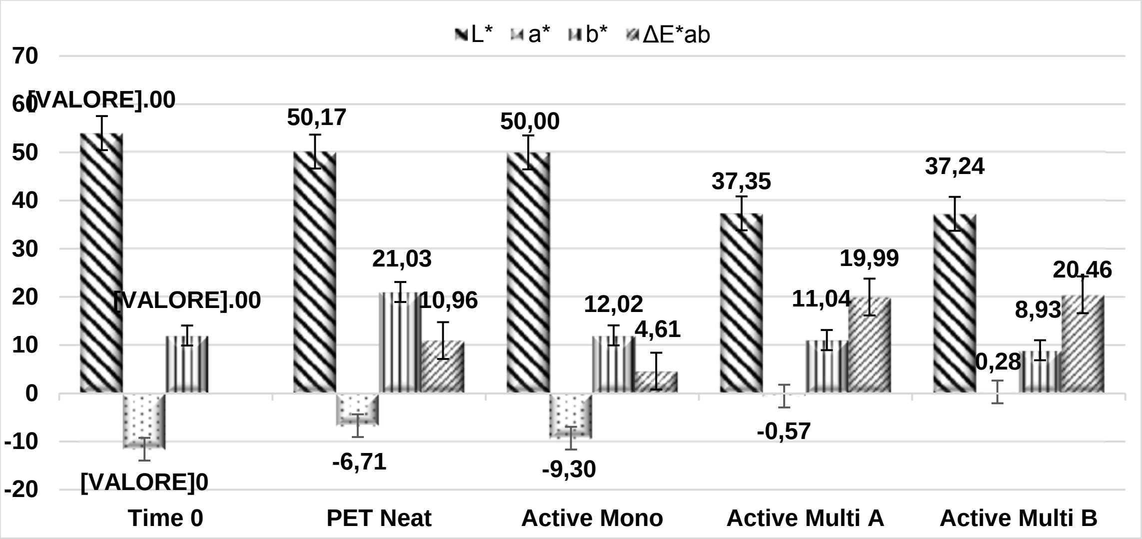

Figure 2: L, a*, b* and ΔE^*_{ab} parameters for broccoli samples stored at 5°C for 15 days in PET Neat and Active packages, compared with initial value (Time 0)*

capacity µ (defined as the ratio between the volume of oxygen absorbed by the films during the test and their weight). Results are shown in Table 2. Oxygen absorption kinetics and absorption properties differs among the active films, depending on the configuration of the layers. All active samples reach almost the same residual oxygen concentration, but at different times depending on the thickness of the inert layers.

Active Mono sample shows the shorter exhaustion time (120 h), whereas it is increases for both multilayer films. This result clearly indicates that the PET inert, external layers hinder the scavenger response, protracting its effect during the time. In particular, exhaustion time increases of 37 %, from 400 h (Active Multi A) to 550 h (Active Multi B), by increasing the thickness of the layers of almost 74 %.

On the other side, it is possible to observe a decrease in scavenging capacity of multilayer samples, if compared the one of Active Mono: this behaviour is explained by the influence of the inert layers on the total weight of the samples, which increases by increasing their thickness.

In order to verify the effectiveness of the active films in preserving the quality of oxygen sensitive foods, preliminary shelf life tests were performed on fresh-cut broccoli florets. Broccoli have a limited shelf life because of their relatively high metabolism rate. Broccoli heads deteriorate rapidly after harvest, and its visual and organoleptic qualities greatly depend on its storage conditions. In order to lower the metabolism of the vegetable and extend its shelf life, it is recommended to decrease the oxygen concentration in the headspace of the package (Izumi et al., 1996). An active device can quickly modify the gas composition inside the packaging, and can be combined with the fruit metabolism to control the equilibrium of oxygen in the headspace around the product (Adobati et al., 2015).

Colour is one of the most important quality attributes of broccoli (Shouten et al., 2009). Yellowing due to senescence of broccoli florets is the main external quality problem in the broccoli production chain, and it is caused by caused by sepal chlorophyll degradation (Corcuff et al., 1998). For this reason, colour of broccoli florets was measured in order to evaluate and quantify chromatic alterations undergone by the vegetables during the storage in active bags. Figure 2 shows L*, a*, b* parameters for broccoli samples after storage at 5°C for 15 days in PET Neat and Active Mono, Multi A and Multi B packages. ΔE^*_{ab} was evaluated for each sample, in comparison with Time 0. Broccoli stored in PET Neat package show the most consistent increase in b* coordinate, which indicates a consistent yellowing of the sample. Florets stored in Active Mono bag show the best overall performances, regarding the retention of green colour (a* value), lightness (L* value) and the yellow colour (b* value), which remain almost unaltered during the storage. Vegetables stored in multilayer active systems tends to a general browning, marked by the increase in a* value, and the decrease of L* value.

Looking at the oxygen absorption curves (Figure 1) and considering the high respiration rates and the oxidative phenomena occurring into the vegetable, it is reasonable to hypothesize that the gas absorption velocity of the OS at early times becomes relevant in this case. The vegetable requires a rapid oxygen reduction (as the one of Active Mono sample), instead of the gradual oxygen reduction offered by the active multilayer samples, in order to maintain its brilliant green colour and visual appearance. This result points out the necessity to design packaging systems basing on individual requirements of the food, in terms of respiration rates, sensitivity to environmental parameters and shelf life parameters.

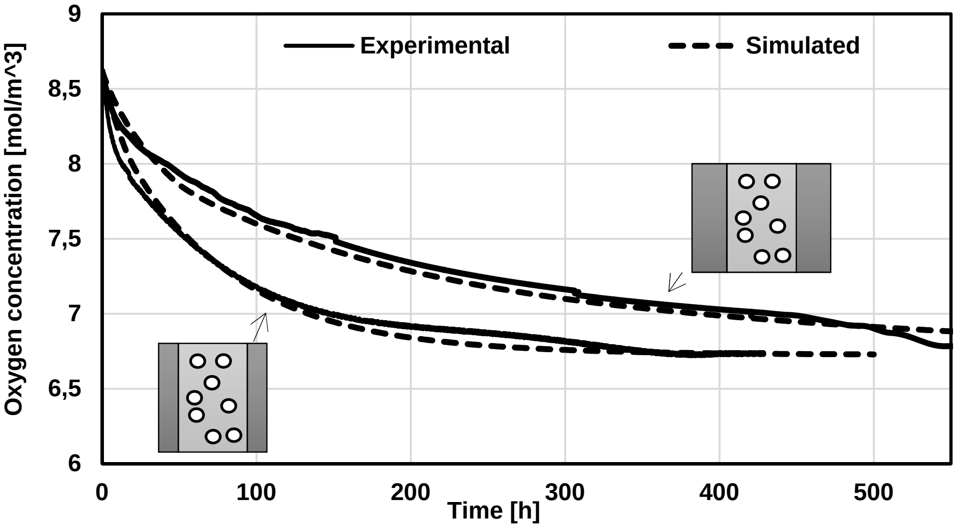

Figure 3: Model validation: comparison of experimental and simulated oxygen absorption curves for Active Multi A and Active Multi B configuration

Finally, a mathematical model was applied to the data set in order to verify its effectiveness in predicting the transport phenomena occurring in the active systems. Mathematical modelling of oxygen scavenging process in polymeric films should take into account both physical and chemical phenomena involved, such as the physical dissolution and diffusion of the gas through the polymer and the reaction of oxygen with the active phase (Gillen and Clough, 1992). Many authors developed mathematical models in order to predict the barrier and scavenging performance of OS-polymer blend films (Ferrari et al., 2009) and multilayer films (Solovyov and Goldman, 2006; Carranza et al., 2012). Scavenging performances of the films depend on a number of parameters, such as the diffusion and solubility coefficients, the concentration of the OS added to the polymer, the number of sites available for the oxidation reaction, as well as the thickness of the layers. Virtualization could be useful to understand the impact of these parameters on the properties of the active films, and could represent a useful tool for characterization, designing and optimization of their scavenging activity.

Figure 3 shows the comparison between experimental and simulated oxygen absorption curves for multilayer samples Active Multi A and Active Multi B. As it is possible to observe, simulated oxygen absorption curves show an immediate reaction of the samples with the oxygen, whose concentration decreases up to reach a plateau value, in correspondence of the relative exhaustion time, dependent on the configuration of the multilayer films. The scavenging activity in the active layer is mainly dependent on the amount of OS concentration loaded in the matrix and, therefore, the number of active sites found in the matrix of the film.

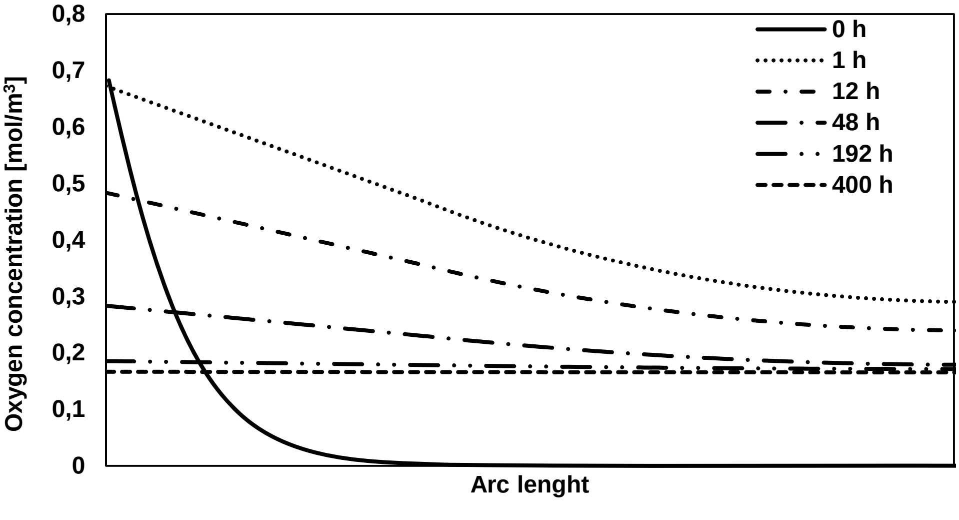

Figure 4: Oxygen concentration profiles from external surface towards the symmetry axis, at different times, for Active Multi A film taken as an example

This characteristic was determined by backward modelling technique using the experimentally measured values. Figure 4 shows Oxygen concentration profiles from external surface towards the symmetry axis, at different times, for Active Multi A film. As shown in the figure, the concentration of oxygen tends to decrease as the oxygen diffuses through the inert layer, up to reach the boundary of the active layer, where the scavenging activity starts. Increasing the time, diffusion occurs through the inert layers until linear profile of oxygen concentration gradient is developed. At the same time, the oxygen concentration in the active layer shows gradual increase because of the scavenging exhaustion, and it remains uniform across the layer at infinite time when the scavenger activity is completely exhausted.

4. Conclusions

PET active symmetrical 3-layer structures were produced by using a cast co-extruder equipment, adding the oxygen scavenger to the central layer. Two multilayer films were obtained by keeping constant the thickness of the active layer and varying the thickness of the inert layer, in order to evaluate the overall scavenging performances of the films, and to compare them with ones of the monolayer films. Oxygen absorption measurements in continuous highlighted the effectiveness of the inert layers in prolonging the scavenging activity of the films, avoiding their rapid exhaustion. Moreover, an increase in exhaustion time lag by increasing the thickness of the inert layers was observed. Preliminary shelf life tests conducted on fresh-cut broccoli florets confirmed the helpful role of the oxygen scavenger in retarding oxidation reactions, thus inhibiting vegetable senescence. Results also pointed out the necessity of designing the food package basing on the requirements of each food, in terms of respiration rates, sensitivity to environmental parameters and shelf life parameters. Finally, the simulation results obtained by mathematical model agreed with the experimental data, highlighting the efficacy of the model in predicting the scavenging activity of the multilayer films and its utility for characterization, designing and optimization of their scavenging performances.

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