Introduction

The improvement of barrier performance of polymers has attracted a great deal of attention in the last decades, as it represents a primary function for those materials involved in packaging of perishable foods, shelf life extension and maintenance of food quality and safety.
The lower limit of definition for high barrier typically refers to the performance of polyethylene terephthalate (PET). PET has become a dominant material for food packaging, thanks to the good barrier properties against oxygen, moisture and carbon dioxide, the extremely low migration of monomers, and the favorable recyclability of post-consumer packages [1]-[3]. However, the increase of the PET barrier performance often becomes compulsory for the packaging of oxygen-sensitive foods and beverages. The entry of even small amount of oxygen into the package, in fact, may deteriorate the product taste and safety [4]-[5]. The development of active packaging, through the addition of oxygen-scavengers (OS), represents an innovative and pursued strategy in order to fulfill more stringent barrier requirements for PET [6]-[10]. The effectiveness of the oxygen scavenger added to the polymer matrix, with the advantage of being tunable in terms of volume of oxygen absorbed, can be enhanced by PET blending with high barrier constituents (mainly aromatic polyamides), which further reduce the amount of oxygen permeating from the environment and simultaneously extend the exhaustion time of the scavenger [1]-[4], [11]-[18].
Since it has been recognized that both PET-oxygen scavengers and PET-aromatic polyamides blends have given good results in terms of barrier properties, the aim of this research is to combine these two approaches, thus developing active polyester films with a double-phase polymeric oxygen scavenger, containing both a copolyester-based O_2-scavenger phase and a copolyamide-based passive-barrier phase, claimed to provide enhanced protection from gas diffusion for a wide range of foods and beverages [19].
Films were produced at different concentrations of the oxygen scavenger by cast extrusion process, and the effects of the system composition on the crystallization behavior, the morphology and the oxygen absorption kinetics of the films were investigated. Moreover, preliminary shelf life tests were conducted to evaluate the effectiveness of the films in preserving sensitive food matrices, using cooked ham slices as test food.

Experimental

The materials are PET Cleartuf P60 (M&G Polimeri, Patrica, Italy), as polymer matrix, and Amosorb SolO_2 (named SOLO, Colormatrix Europe, Liverpool, UK) an auto-activated polymeric oxygen scavenger designed for PET bottles and food contact approved from FDA and EU legislation. The scavenger is characterized by the presence of a double phase: a violet, active phase, of copolyester nature, which effectively reacts with the oxygen (named SOLO_V), and a white phase of copolyamide nature, which gives enhanced gas barrier properties (SOLO_W) [19]. The measured weight percentages for the violet and white phases inside Amosorb SolO_2 are 60% and 40%, respectively.
Before processing, the PET was dried under vacuum at 130 °C for 16 h, to avoid hydrolytic degradation. The SOLO, delivered in aluminum bags sealed under vacuum, was used as received. Single layer active PET films were produced by a laboratory cast film extrusion equipment, by adding the oxygen scavenger at 0, 5%, 10% and 20% by weight. The extruder was equipped with a screw having diameter of 12 mm and an L/D ratio of 24. The extrusion flat die had lip width of 200 mm and thickness of 0.25 mm. The extruder temperature profile was set at 280°C along the extruder and at 270°C at the die.

Scanning Electron Microscopy (SEM) analyses were conducted to investigate the morphology of the produced films. Film sections were cut cryofracturing them in liquid nitrogen normally to the extrusion direction, sputter coated with gold (Agar Auto Sputter Coater mod. 108A, Stansted, UK) at 30 mA for 160 s, and analyzed using a field emission scanning electron microscope (mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany). Sigma Scan Pro 5.0 (Jandel Scientific, San Rafael, Canada) was used for image analysis.
Thermal analyses on the produced films were performed using a Differential Scanning Calorimeter (DSC mod. 822, Mettler Toledo). Experiments were carried out under nitrogen gas flow (100 ml/min) in order to minimize thermo-oxidative degradation phenomena. The samples were first heated at a rate of 10°C/min, from 25°C to 300°C, and held at this temperature for 5 min to allow the complete melting of the crystallites; then they were cooled from 300°C to 25°C at a rate of 10°C/min. The values of glass transition, cold crystallization and melting temperature (T_g, T_{cc}, T_m), the enthalpy of cold crystallization and melting (ΔH_{cc} and ΔH_m) and the percentage of crystallinity (Xc) were evaluated from the first heating scan; the values of crystallization temperature and enthalpy (T_c, ΔH_c) were calculated from the cooling scan. Xc was calculated according to the Equation (1):

$$Xc = \frac{\Delta H_m - \Delta H_{cc}}{(1 - w) * \Delta H_\infty} \quad (1)$$

where ΔH_∞ is the heat of melting of purely crystalline PET, equal to 140 J/g [20], and w represents the weight fraction of active phase.

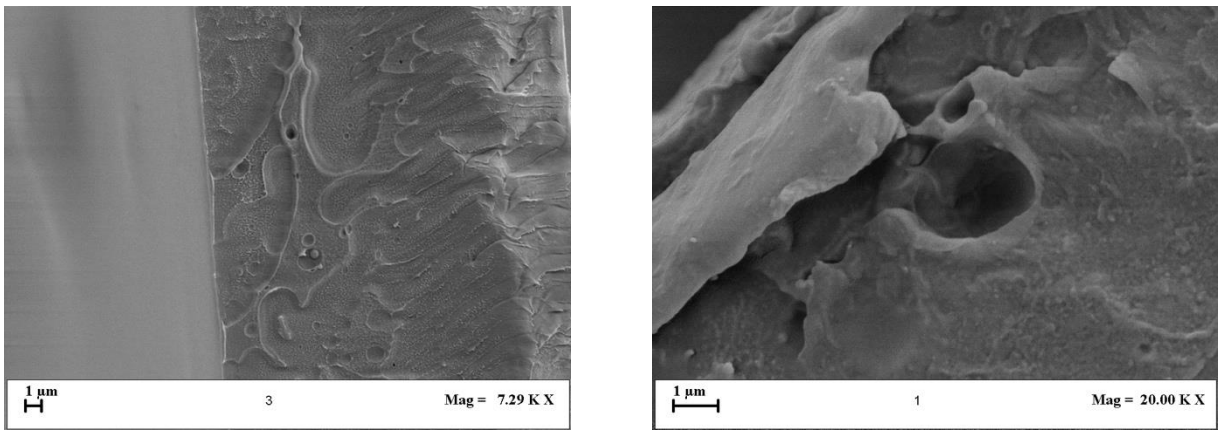
Oxygen absorption measurements were carried out at 25 °C in continuous mode by means of the fiber optical oxygen meters Minisensor Oxygen Fibox 3-Trace V3 and Stand-alone Oxygen Meter Fibox 4 (PreSens GmbH, Regensburg, Germany), equipped with a polymer optical fiber and oxygen sensor spots SP-PSt3-NAU (detection limit 15 ppb, 0–100% oxygen). Experiments were conducted on cut film samples with a defined geometry (8.0 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. From the oxygen absorption curves, it was possible to calculate the main absorption properties of the active films, such as the total volume of oxygen absorbed V_{Ox}, the exhaustion time t_E (i.e. as the time at which the O_2 concentration becomes constant), and the scavenging capacity μ, calculated as the ratio between the total volume of oxygen absorbed and the weight of the films.

The effectiveness of the active films in extending the shelf life of oxygen-sensitive foods was verified by preliminary shelf life tests, using slices of cooked ham as test food. Ham was purchased on the local market, and stored at 4 ± 1°C overnight before slicing and packaging. On the day of packaging, the ham was cut in slices of (10 x 10) cm^2 area and 0.3 cm thickness, and individually sealed inside the bags made of neat and active PET. After packaging, samples were stored at 4 ± 1°C, both in illuminated (24 h/day) or in darkness conditions. A LED light with natural light (4000 K), luminous intensity equal to 750 lumens and an emission angle of 120° was used as light source. The red color of ham slices was measured by means of a tri-stimulus colorimeter Minolta CR-300 (Konica Minolta International, Japan), and the CIE Δa* parameter ($\Delta a^* = a^*_t - a^*_{t=0}$) was calculated. The measurements were taken on the ham slices by opening the packaging films at 1, 3 and 7 days,

and 2 different locations on the ham surface were measured. Measurements were performed in triplicate.

Results and discussion

The distribution and dispersion of the active phase inside the polymer matrix was investigated through SEM analyses. (Figure **1** shows the cross-section micrographs of the active films at 5% and 20% of the oxygen scavenger.



(A) (B)

(Figure 1 SEM micrographs of: (A) PET + 5% SOLO film; (B) PET + 20% SOLO film.

As expected, the presence of the polymeric oxygen scavenger inside the PET matrix is highlighted by the occurrence of spheroidal domains, which size and arrangement vary depending on the composition of the samples [7]. In particular, the films at low percentage of SOLO show an uneven layout of the OS particles, which diameter is less or equal to 1 micron ((Figure **1** (A)), while the film at 20% of SOLO shows the presence of big voids related to OS aggregates with diameter larger than 1 micron ((Figure 1 (B)).

DSC analyses were carried out on the films to investigate the effect of the different percentages of active phase on the crystallinity behavior of the polymer matrix, and the results are reported in Table 1. Thermal tests were also conducted on the OS pellets, in order to obtain more information about their thermal transitions.

The DSC data confirm the copolyester nature of the violet phase SOLO_V of the oxygen scavenger, which shows a single melting peak, at a temperature of 248°C, comparable to the one of neat PET. On the other hand, the white phase SOLO_W shows two melting peaks - the first one, quite small, centered at c.a. 194°C, which falls within the melting range of polyamides [21], and the second one at 239°C - suggesting a more complex nature of both copolyester and copolyamide composition. For all the active films, instead, only a single melting peak is observable, at Tm around 250°C, while the melting peak imputable to the copolyamide phase is no longer appreciable, due to the small concentrations of OS dispersed inside the polymer matrix.

Moreover, with respect to the PET film, all active systems feel the nucleating effect of the oxygen scavenger. Therefore, it can be observed a slight crystallinity increase from 9% to 12% at increasing SOLO amount, a slight decrease of the cold crystallization temperature Tcc, and the shift of the crystallization temperature Tc towards higher values, whose significance increases by increasing the percentage of OS.

Table 1 Thermal parameters of the active films and of the active pellets, related to the heating and cooling cycles.

Sample	First heating						Cooling	
	T_g [°C]	T_{cc} [°C]	T_m [°C]	ΔH_{cc} [J/g]	ΔH_m [J/g]	X_c [%]	T_c [°C]	ΔH_c [J/g]
SOLO_V	*n.d.*	*n.d.*	248	*n.d.*	38.8	*n.a.*	159	25.2
SOLO_W	*n.d.*	*n.d.*	194; 239	*n.d.*	2.8; 56.9	*n.a.*	182	40.3
Film PET	78	134	253	32.5	44.8	9	192	40.7
Film PET + 5% SOLO	77	134	252	32.1	46.6	11	197	42.8
Film PET + 10% SOLO	77	133	251	31.6	45.9	11	199	42.2
Film PET + 20% SOLO	76	131	250	34.3	47.3	12	200	43.5

n.d. = not detectable; n.a. = not applicable

Oxygen absorption measurements in continuous were performed in order to evaluate the oxygen scavenging capacity and the absorption rate of the active films produced. The obtained curves are compared in Figure 2 and the scavenging parameters calculated from the curves are listed in Table 2.

The oxygen absorption kinetics of Figure 2 show an immediate reaction of all the active films with the oxygen inside the vial, absorbing it during the time, up to reach the film exhaustion displayed by the plateau stage. At short times, the oxygen absorption rate increases inversely proportional to the OS concentration. The phenomenon can be due to the presence, in the OS formulation, of the copolyamide phase that, acting as passive gas barrier, the more hinders the oxygen diffusion towards the reactive sites, the higher is the OS loading. At long times, the absorption kinetics progressively slow down up to activity exhaustion. In particular, the PET film at lowest SOLO content shows the lowest scavenging capacity (2.02 cc O_2/g film) and the shortest exhaustion time (about 70 hours). As expectable, the film at 10% SOLO has an almost double scavenging capacity and a much longer exhaustion time, thanks to the higher amount of copolyamide phase as passive barrier that delay the oxygen diffusion across the film. Otherwise, the film at 20% SOLO shows only a small increase of scavenging capacity and a reduction of the exhaustion time with respect to the film at 10% of SOLO. This result is related to the little homogeneous film morphology, characterized by the presence of large particles of OS phase. This leads to a slowing of the absorption rate, due to the fewer reactive sites exposed on the surface and a more difficult O_2 diffusion towards the inner reactive sites, causing a premature depletion of the film.

These results are coherent with those obtained in our previous studies on other active PET films containing a different OS, where it was found that the scavenging performance depens not only on the percentage of oxygen scavenger added, but also on the morphology developed upon processing in terms of dispersion, distribution and size of the active phase [7],[10].

Table 2 Exhaustion time t_E, total volume of oxygen absorbed V_{O2} and scavenging capacity μ for PET films loaded at different percentages of oxygen scavenger.

Sample film	t_E [h]	V_{O2} [cc]	μ [cc O_2/g film]
PET + 5% SOLO	70	0.19	2.02
PET + 10% SOLO	650	0.34	3.93
PET + 20% SOLO	250	0.56	4.48

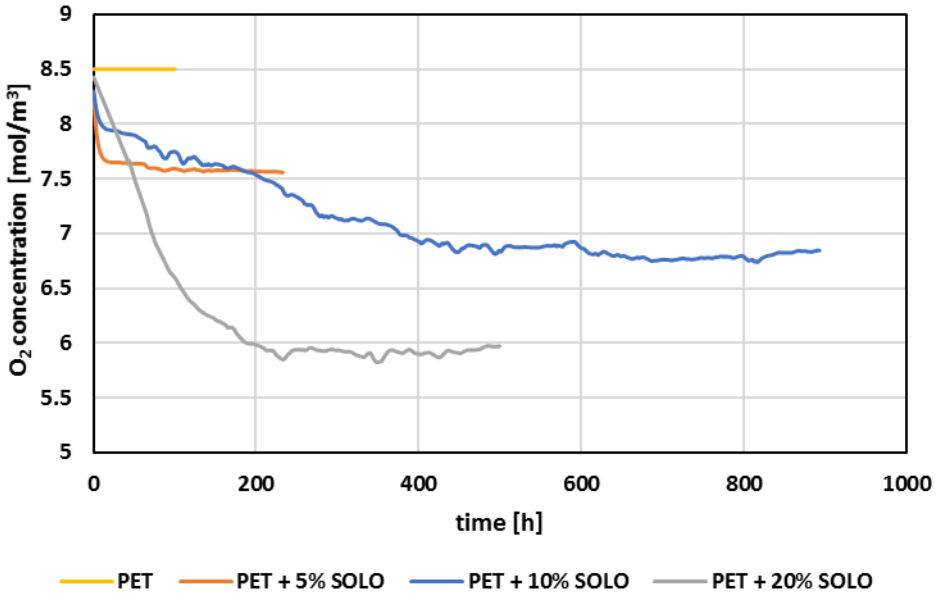


Figure 2 Oxygen absorption kinetics at 25°C for the active films at different percentages of oxygen scavenger compared with PET film.

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 slices of cooked ham.

For meat products, color is one of the most important aspects that influences the purchase and the assessment of quality and palatability. Several works pointed out the oxygen impact on discoloration of cooked ham, due to the oxidation of denatured nitrosomyoglobin (dMbNO) to metymioglobin (MMb), catalyzed by the presence of light, resulting in a grey color of the product surface [22]-[25].

This discoloration is reflected in a decrease in the value of the CieLab a* parameter, which has been investigated through colorimetric measurements. For this purpose, Figure 3 shows the changes in redness ($\Delta a^* = a^*_t - a^*_{t=0}$) for all the samples with the different packaging films and storage conditions.

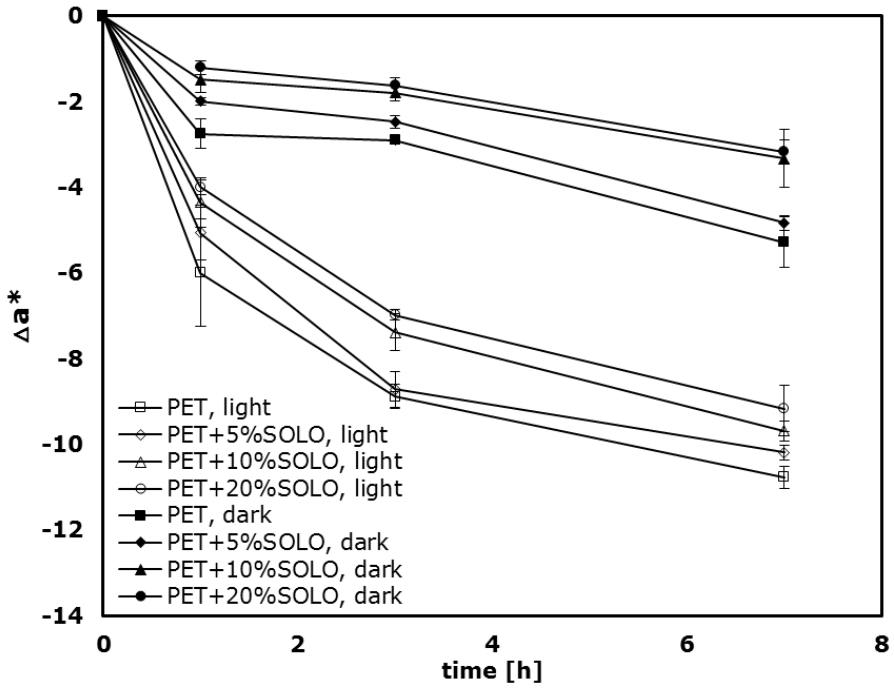


Figure 3 Changes in redness ($\Delta a^* = a^*_t - a^*_{t=0}$) of ham slices packaged in neat PET and active films at different percentage of oxygen scavenger, during 7 days storage at 4 ± 1°C. Color of the symbols indicate whether the samples were stored in dark (black) or illuminated conditions. Mean value ± standard deviation.

All illuminated samples show a quick discoloration, started since early times after packaging, as well as the most significative decrease in Δa* parameter, pointing out the crucial role of light in catalyzing the oxidative reaction, as also confirmed by other authors [22]-[24].
On the other side, all the samples stored in darkness show a less pronounced decrease in redness, especially between day 1 and 3, during which the a* parameter is almost constant for all the films. The maximum discoloration rate is observed, in both cases, between day 0 and day 1, indicating that the product just cut and packaged is very sensitive to environmental conditions, while instead, in the following two days, the darkness condition favors a slowing of the discoloration reaction, such that the a* parameter remains almost constant.
Moreover, samples stored in neat PET, both in light and dark conditions, exhibit the most consistent graying, while a better color retention is observed for samples stored in active films by increasing the scavenger percentage, with the best behavior for the film at 20% SOLO. These results can be explained taking into account the oxygen absorption curves seen before, particularly in the first 200 hours, in which it is clear how the 20% SOLO system rapidly lowered the oxygen concentration inside the headspace of the pack, effectively slowing down the ham discoloration, pointing out the importance of scavenger absorption kinetics to extend the durability of the foods depending on the specific requirements.

Conclusions

Single layer, active PET films were produced at different concentrations of a double phase oxygen scavenger, copolyester and copolyamide-based, by cast extrusion process.
SEM images showed the effect of the amount of OS added and of the processing conditions on the morphology of the PET samples, playing a crucial role on the final scavenging performance of the films and on their oxygen absorption kinetics.

Thermal analyses highlighted the influence of the scavenger phase on the crystallization behavior of the polymer matrix, acting as a nucleating agent.
The results of oxygen absorption measurements highlighted that the 10% scavenger concentration was the best in terms of dispersion and distribution of the reactive domains inside the PET matrix, leading to the best performance of the film in terms of prolonged exhaustion time. Increasing the scavenger content up to 20%, instead, the occurrence of larger domains poorly dispersed inside the polymer matrix leads to a premature exhaustion of the film.
Finally, preliminary shelf life tests conducted both in light and dark conditions on cooked ham slices showed the potential of the active films in retarding the oxidation reactions, thus prolonging the shelf life of sensitive food matrices.

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