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Oxygen scavenging films for food application

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Abstract

The presence of oxygen causes deterioration of oxygen-sensitive foodstuffs. This leads to a deterioration of quality characteristics like colour, freshness and organoleptic properties. Due to the strong influence of temperature and exposure to light (photo-induced oxidation processes) this effect especially appears in transparent packaged chilled products (like sausages). Therefore, it is necessary to reduce the oxygen content in the headspace of the package. One possibility is the use of modified atmosphere packaging (MAP). But even at optimised processes the residual oxygen-concentration is up to 0.5 – 2 %. To reduce this destructive oxygen, the additional use of oxygen scavengers becomes more and more attractive. Fraunhofer Institute for Process Engineering and Packaging worked together with industrial partners on an improvement of the kinetics of oxygen scavengers. In the AiF-funded project "Optimisation of transparent packaging materials with iron-based oxygen-scavengers for chilled products" (Nr. 15555N) the kinetics of oxygen-scavengers should be improved. Background of this was that the systems that are already available at the market do not work fast enough at low temperatures (5 °C). Therefore the aim of the project was to incorporate the oxygen scavenger into the packaging material and thus achieving better quality preservation and longer shelf-life of the chilled food. It could be shown that integrating the masterbatch SHELFPLUS® 2500 (SP2500) in a polymer (EVA) with high oxygen permeability resulted in higher oxygen consumption. Comparisons of the oxygen consumption of sausage and film showed that the use of the multilayer film PE/AL(SP2500; EVA) in combination with the food (exposed to light) resulted eight days earlier in a total consumption of the oxygen than storing the sausage without active film. This leads to a certain protection of the sausage.

Keywords: oxygen scavenger; active packaging; chilled products; sausage

1. Introduction

Many foods like sausages or cheese are very sensitive for oxygen and light. This leads to oxidation reactions with fatty acids and under presence of light also to a destruction of pigments (photo-oxidation),

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e.g. nitrosomyoglobin in sausages. Discolouration and rancidity are the consequences that lead to a rejection of the product by the consumer [1]. Therefore the food has to be protected against oxidative changes, preliminary caused by photo-oxidation. This can be achieved by packaging the food in non-transparent packages and under a modified atmosphere (MAP-Modified Atmosphere Packaging). Previous investigations [2] showed that sausages are mainly packaged in an atmosphere with a mixture of CO_2 and N_2. But even at optimised processes the residual oxygen-concentration is up to 0.5 to 2 %. This is due to oxygen that remains in the headspace after packaging process or due to solved oxygen in the food permeating into the headspace. Under presence of light even these low oxygen concentrations are enough to achieve undesired colour and odour changes. Because of the consumers demand for transparent packages an exclusion of light is not possible. Therefore the rest-oxygen content has to be reduced. A good way might be the use of oxygen scavenger systems [3; 4; 5]. There are already different systems available on the market like iron-based systems for ready-to-serve meals or natrium-sulfit based systems for beverages [3; 4; 5; 6; 7]. But these systems do not work fast enough at low temperatures (5 °C) to effect a protection of the chilled food. Predominantly colour changes are the consequence. Therefore efforts are made to optimise iron-based oxygen-scavenger systems to make them usable for application with chilled foods. The incorporation of the iron and additives in polymers with high oxygen and water vapour permeabilities is a comprising approach.

2. Materials & Methods

2.1. Production of oxygen scavenger multilayer films

Oxygen scavenging films (PE/AL(active layer)) were produced at the Fraunhofer Institute on an extrusion facility (Dr. Collin GmbH, Ebersberg, Germany). The oxygen scavenger masterbatches SHELFPLUS® (SP) 2400 and 2500 (now owned by Albis Plastic GmbH, Hamburg, Germany, former owner Ciba® Speciality Chemicals Inc., Switzerland) [8] were used. The masterbatches contain iron powder and different additives and are activated at a relative humidity (RH) above 70 % [9]. Following polymers were used for producing the films: PE, PP and EVA.

Three different active films were produced:

(a) PE (20 µm)/AL(SP 2400; PE) (30 µm)

(b) PE (20 µm)/AL(SP 2500; PP) (30 µm)

(c) PE (20 µm)/AL(SP 2500; EVA) (30 µm)

The active layer (AL) was produced by mixing one mass fraction of the oxygen scavenger masterbatch with one mass fraction of the polymer.

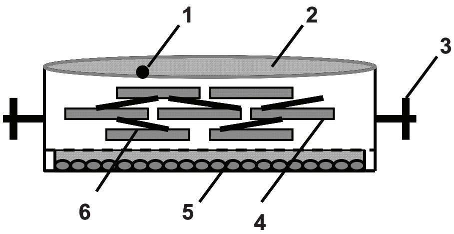
2.2. Measurement of the oxygen absorption

To characterise the oxygen absorption of the oxygen scavenger films measuring cells were used (Figure 1) [10]. The cells were made of stainless steel with two valves to flush the cell with a desired gas. The gas mixture consisted of 0.5 % O_2 and 99.95 % N_2 (Linde Gas, Germany). Measuring cells had an inner diameter of 9 cm and thus a permeation area of 63.6 cm^2. To adjust the oxygen ingress rate the measuring cells were sealed after filling with a high barrier lid film (PET/SiOx/BOPA/PP). To analyse the absorption of the oxygen scavenger, 350 cm^2 of the scavenging film (cut in pieces of 5x5 cm) was adhered to an aluminium foil to guarantee an oxygen permeation only by one side (outer side: AL or PE). Then the samples were placed into the measuring cells with 10 ml distilled water to an adjusted relative humidity (RH) of 100 %. Spacers made of PP were used to separate the pieces to allow free access of headspace gas to the surface of the film.

Food samples were taken from freshly produced packages. To analyse the absorption of the sausages 70 g of the food was placed in measuring cells. The samples were cut and put into the measuring cells under a clean bench. The RH was adjusted by the food itself (92 %). On the inside of the lid film an optical sensor (SP-PSt6-NAU-D5-YOP; PreSens Precision Sensing GmbH, Regensburg, Germany) was placed to measure the oxygen concentration with time. The oxygen concentration was measured via fluorescence behaviour (Fibox 3-trace; PreSens Precision Sensing GmbH, Regensburg, Germany). Cells were stored at 23 °C or 5 °C, 50 % RH in air (21 % O_2). The oxygen consumption (V_c) of the samples was calculated using following equation:

$$V_c = V_{O2,headspace,t=0} + V_{O2,permeation,t=x} - V_{O2,headspace,t=x} \quad (1)$$

$V_{O2,headspace,t=0}$: initial oxygen volume in the headspace
$V_{O2,permeation,t=x}$: the volume of oxygen that permeates into the measuring cell (t=x)
$V_{O2,headspace,t=x}$: the volume of oxygen at t=x



1: oxygen sensor
2: lid foil with defined oxygen ingress
3: valves
4: sample
5: dish with distilled water
6: spacer

Fig. 1: measuring cell [11]

2.3. Calculation of error bars

The error bars in the following figures (results and discussion) show standard deviation based on 3-fold measurements.

3. Results & Discussion

3.1. Influence of temperature on the oxygen consumption of the oxygen scavenger

As chilled products are stored under low temperatures (5 °C) the influence of temperature on the oxygen consumption velocity of an oxygen scavenger film was investigated. The oxygen absorption of the multilayer film PE/AL(SP2400; PE) was investigated at two different temperatures (5 °C; 23 °C) at an initial oxygen concentration of 0.5 % in the headspace of the measuring cell and a RH of 100 %.

Figure 2 shows the oxygen consumption [cm3O2/m2film] of the scavenger films (outer side: AL). The film stored at 23 °C absorbed the oxygen in the headspace 3.0 times faster (within the first 4 days) than the samples stored at 5 °C. Both curves reach after 15 days almost the same level of oxygen consumption (about 33 cm3O2/m2film). Further investigations on iron-based oxygen scavenger systems agree with the conclusion that the oxygen consumption of iron-based oxygen scavenger films increase with increasing temperature [7; 9; 12; 13].

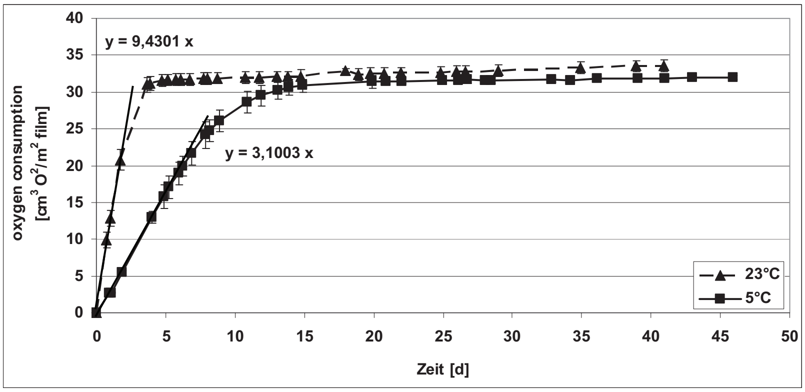


Fig. 2. Influence of temperature on the oxygen consumption of an oxygen scavenger multilayer film (PE / AL(SP2400;PE); outer side: AL; at RH 100 %) [11]

3.2. Influence of the masterbatch mixture on the oxygen consumption

For packaging chilled foods PP-trays with SP2500 are in common use. SP2400 with its higher oxygen consumption rate compared to SP2500 is not compatible with PP. A new approach was to use the polymer EVA (with a higher oxygen permeability) instead of PP together with the masterbatch SP2500 to generate a higher oxygen transmission rate. To investigate the influence of the polymer on oxygen consumption three different films were stored in measuring cells (outer sider: PE) at 5 °C, 100 % RH and an initial oxygen concentration in the headspace of 0.5 %:
(a) PE/AL(SP2500; EVA); (b) PE/AL(SP2500; PP) and (c) PE/AL(SP2400; PE).

Figure 3 shows the oxygen consumption [cm^3O_2/m^2film] of the investigated films. The masterbatch SP2500 was incorporated into EVA (a) and into PP (b) to form the active film. The oxygen consumption of film (a) was 2.3 times faster than the oxygen consumption of film (b). This can be explained by the higher oxygen permeability of the polymer EVA compared with PP (by factor 2.3) [14]. Almost the same oxygen consumption rate of films (a) and (c), which is mainly used for flexible films, were measured within the first few days.

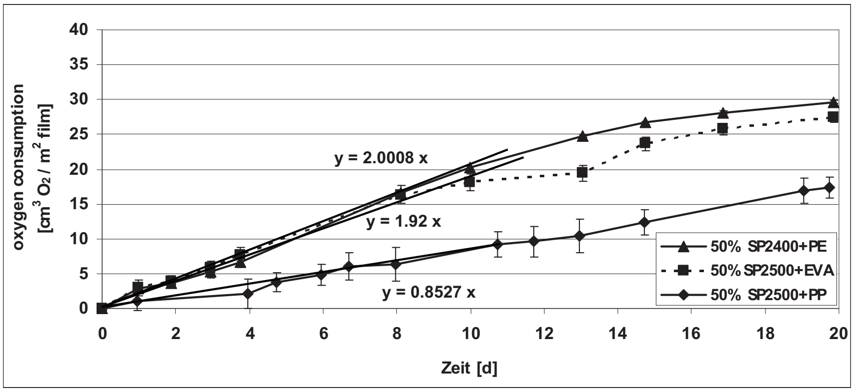


Fig. 3. Influence of incorporating the scavenger masterbatch in different polymers to the oxygen consumption; at 5 °C and a RH 100 % [11]

3.3. Oxygen consumption of sausage compared with active film

Figure 4 shows as comparison the oxygen concentrations [%] in the headspace of the measuring cells with film (a), the food sample (sausage) and additionally the calculated combination of scavenger film and sausage. The samples were stored at 5 °C with an initial oxygen concentration in the headspace of the measuring cell of 0.5 %. During storage the sausage was exposed to light (about 850 lux; 12 hours/day) to simulate retail conditions.

During the first day of storage the measuring cells with sausage showed an increase of oxygen concentration to about 0.8 %. This is due to solved oxygen in the food [15]. The initial oxygen concentration of the measuring cells with multilayer film also increased (up to 0.6 %), due to solved oxygen in the polymer and distilled water. Subsequently both, the scavenger film and the food note a decrease in oxygen concentration. The calculated curve of the combination (scavenger film and sausage) shows the fastest decrease in oxygen concentration. Since oxygen free conditions were achieved 8 days earlier compared to the storage of the sausage alone, a certain protection of the sausage could be concluded.

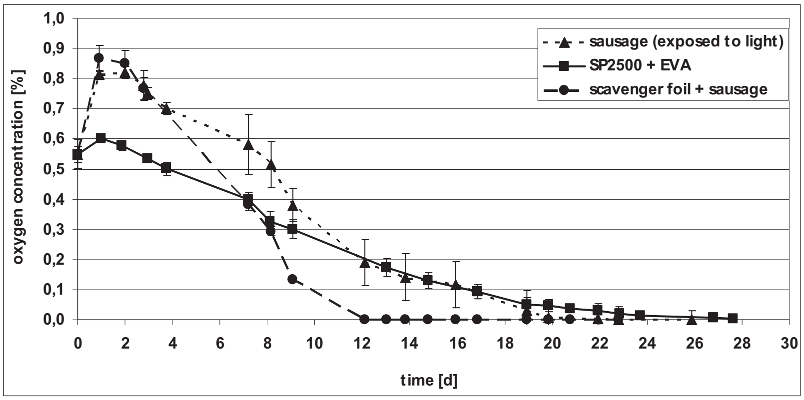


Fig. 4. Comparison of oxygen concentration in measuring cells with oxygen scavenger film, sausage (exposed to light) or their combination; at 5 °C [11]

4. Conclusion

First investigations concentrated on defining the influence of temperature to the oxygen consumption of an oxygen scavenger film. Reducing the temperature from 23 °C to 5 °C caused a decrease (factor 3.0) in the oxygen consumption rate of the oxygen scavenger multilayer film PE /AL(SP2400; PE) within the first four days (RH 100 %; 0.5 % initial headspace-oxygen).

Moreover the influence of using a polymer with a higher oxygen permeation rate than PP (commonly used) to the oxygen consumption of the scavenger film was investigated. Thus the masterbatch SP2500 was mixed with EVA that shows higher oxygen permeability than PP (by factor 2.3). Consequently the oxygen scavenger multilayer film PE/AL(SP2500; EVA) showed a faster oxygen consumption than the film PE/AL(SP2500; PP) (by factor 2.3).

Finally the oxygen concentration in measuring cells with scavenger film PE/AL(SP2500; EVA) and with sausage were compared at 5 °C (initial oxygen concentration in headspace: 0.5 %). The combination (calculated) with oxygen scavenger film showed a faster oxygen decrease in the headspace of the measuring cell than the sausage alone. This leads to the assumption of a certain protection of the sausage against oxygen deterioration. Better protection of the sausages might be achieved by storing the food sample in combination with the scavenger film in darkness for the first few days. This would allow the scavenger to absorb the oxygen much faster than the sausage because the fast photo-oxidation processes in the food do not appear without light-exposure.

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