Food Packaging and Shelf Life 8 (2016) 56–62

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

journal homepage: http://www.elsevier.com/locate/fpsl

Use of palladium based oxygen scavenger to prevent discoloration of ham

Simon Hutter, Nadine Rüegg, Selçuk Yildirim*

Zurich University of Applied Sciences, Institute of Food and Beverage Innovation, Waedenswil, Switzerland

ARTICLE INFO

Article history:
Received 25 September 2015
Received in revised form 16 February 2016
Accepted 26 February 2016
Available online 4 April 2016

Keywords:
Oxygen scavenger
Palladium
Active packaging
Discoloration
Cooked cured ham

ABSTRACT

The efficiency of an oxygen scavenging film based on a catalytic system with palladium (CSP) was used to prevent the discoloration of cooked cured ham. Sliced ham was packed under modified atmosphere (2 vol.% O_2, 5 vol.% H_2, 93 vol.% N_2) or normal atmosphere in high barrier trays with or without CSP. Packages were stored for 21 days at 4 ± 1 °C under illumination or in darkness. Samples stored in the dark did not show any discoloration, whereas ham stored under illumination showed a pronounced loss in redness. In packages with the CSP, the headspace oxygen concentration of 2 vol.% was removed within 35 min. There was no discoloration observed in samples with CSP although they were stored with 24 h/day illumination. Significant differences ($p < 0.01$) in redness between the illuminated samples with and without CSP could already be observed after 2 h of storage.

1. Introduction

Oxygen can have detrimental effects on the quality of different food products as it promotes growth of aerobic microorganisms (Lee, 2010) and induces oxidation reactions (Choe & Min, 2005). While growth of microorganisms may limit the shelf life and endanger the safety of the product, oxidation reactions may result in a decrease in nutritional value, change of texture, production of off flavors, or change in color of the products (Decker, Elias, & McClements, 2010).

For meat and meat products, color is one of the most important aspects affecting purchase decision and assessment of quality and palatability (Eyiler & Oztan, 2011; Hood & Riordan, 1973; Kostyla, Clydesdale, & McDaniel, 1978). In cooked cured ham, denatured nitrosomyoglobin (dMbNO) formed during curing and cooking is responsible for the pink red color (Andersen, Bertelsen, Boegh-Soerensen, Shek, & Skibsted, 1988; Fox, 1966). In the presence of both light and oxygen, dMbNO is oxidized to metmyoglobin (MMb), which results in a grey brown color on the surface of the ham (Andersen & Skibsted, 1992). This discoloration is reflected in a decrease in CIE a^* value (Andersen et al., 1988; Böhner, Hösl, Rieblinger, & Danzl, 2014; Larsen, Westad, Sørheim, & Nilsen, 2006; Møller, Jensen, Olsen, Skibsted, & Bertelsen, 2000).

The critical oxygen level causing discoloration in ham is between 0.1 and 0.5 vol.% depending on the product/headspace ratio (Böhner et al., 2014; Larsen et al., 2006; Møller et al., 2000; Nannerup et al., 2004). Therefore, ham is often packed using modified atmosphere packaging (MAP) to reduce the oxygen concentration in the headspace (McMillin, 2008). However, due to oxygen trapped in the food matrix or insufficient gas flushing, the residual oxygen concentration in the headspace of MAP products can remain between 0.3 and 3 vol.%, sufficient to cause adverse effects in oxygen sensitive food (Böhner et al., 2014; Gibis & Rieblinger, 2011; Larsen et al., 2006; Pereira de Abreu, Cruz, & Paseiro Losada, 2012). Since meat products on retail shelves are usually packed in transparent films and stored illuminated, the control of the residual oxygen levels in the packaging is of great interest.

Oxygen scavengers can be used to reduce the oxygen concentration in the headspace below 0.1 vol.% (Pereira de Abreu et al., 2012). The most widely used mechanism for oxygen scavengers today is the oxidation of iron or iron salts contained in sachets (Pereira de Abreu et al., 2012). The application of this type of scavenger though is limited because of low oxygen scavenging rates and the limited consumer acceptance of the sachets (Gibis & Rieblinger, 2011; Miltz & Perry, 2005; Pereira de Abreu et al., 2012; Tewari, Jayas, Jeremiah, & Holley, 2002). Meat

* Corresponding author at: Zurich University of Applied Sciences, Institute of Food an Beverage Innovation, Einsiedlerstrasse 34, 8820 Waedenswil, Switzerland. Fax: +41 58 934 50 01.
E-mail address: selcuk.yildirim@zhaw.ch (S. Yildirim).

http://dx.doi.org/10.1016/j.fpsl.2016.02.004
2214-2894/

products packaged with this type of oxygen scavengers usually have to be stored in darkness after packaging for a duration of 10 h up to several days until the oxygen is completely scavenged (Andersen & Rasmussen, 1992; Gibis & Rieblinger, 2011; Nannerup et al., 2004).

Recently an oxygen scavenging film based on a catalytic system with palladium (CSP) has been developed which is able to reduce residual headspace oxygen very quickly (Yildirim, Röcker, Rüegg, & Lohwasser, 2015). Palladium catalyzes the oxidation of hydrogen into water (Nyberg & Tengstål, 1984; Wanner, 2010) and thus can remove the residual oxygen in the headspace of a modified atmosphere packaging containing hydrogen (Yildirim, Jammet, & Lohwasser, 2010; Lohwasser & Wanner, 2005). The CSP, which is an extension to existing MAP technology, can be attached to the inside of the packaging film and is used in conjunction with a modified atmosphere.

Solomon (2004) reported that sliced meat products, such as smoked and cured ham, are the food product category with the largest potential for employing oxygen scavengers. For such products however, oxygen scavengers have to be able to remove the oxygen very fast, since the light-induced discoloration occurs within hours (Andersen & Rasmussen, 1992; Böhner et al., 2014).

In this study, the efficiency of the newly developed catalytic system based on palladium to preserve the color of cooked cured ham was tested. Ham was packed under normal atmosphere (~20.95 vol.% O_2) or modified atmosphere with 2 vol.% oxygen (to simulate residual oxygen) with or without the CSP. Samples were stored in darkness or illuminated (24 h/day) for 21 days. To simulate retail conditions, additional samples with modified and normal atmosphere were stored illuminated for 8 h/day. Oxygen concentration in the headspace and the change in color of the ham were monitored during storage.

2. Materials and methods

2.1. Catalytic system based on palladium (CSP)

Palladium (1.04 nm) was deposited on a PET/SiO_x film (38.5 μm/80 nm) using magnetron sputtering technology as previously described by Yildirim et al. (2015). The CSP was cut into labels (25 cm^2) and one label per package was attached to the inner side of the packaging film.

2.2. Sample preparation, packaging and storage

Vacuum packed cooked cured ham (whole, approx. 4.6 kg) was received from a Swiss industrial meat processor with the following composition: pork 72%, water, nitrite salting mix (salt, preservative: sodium nitrite), aroma, stabilizers: di- and triphosphate, antioxidant: sodium carbonate, glucose, glucose syrup, sugar and spice extract. Nitrite addition during the curing process was 114 ppm. On receipt, the ham was stored at 4 ± 1 °C for 1 day before slicing and packaging. On the day of packaging, the ham was cut in slices with a thickness of 1.5 mm and 2 slices (total weight: approx. 54 g, total volume: approx. 50 ml) per sample were packed. Packages consisted of a PS-EVOH-PE tray (thickness: 0.5 mm, packaging volume: 210 ml, Stäger & Co., AG, Muri, Switzerland) and a 57 μm PET/PE-EVOH-PE lidding film (O_2 transmission rate ≤2.5 cm^3/m^2 d bar at 23 °C and 50% relative humidity; Südpack Verpackungen, Germany). The resulting product to headspace ratio was 1/3.2 [v/v]. Samples were packed with normal (NA, ~20.95 vol.% O_2) or modified atmosphere (MA, 2 vol.% O_2, 5 vol.% H_2, 93 vol.% N_2, Pangas, Dagmersellen, Switzerland) using a traysealer (vacuum: 30 hPa, gas flushing: 980 hPa, Multivac T200, Multivac Export AG, Hünenberg, Switzerland). After packaging, samples were stored illuminated (8 or 24 h/day) or in darkness in a cooling chamber with forced air circulation at 4 ± 1 °C for 21 days. Fluorescent tubes (Lumilux HE 21 W/830 warm light G5, Osram GmbH, Munich, Germany), placed 25 cm above the samples were used as a light source, resulting in a light intensity of 1000 ± 100 lx (1332A Digital lux meter, TES, Taiwan). To ensure a uniform illumination, the position of the packages was changed after every measurement.

2.3. Oxygen measurement

The oxygen content inside the packaging was measured with a non-destructive fiber optic oxygen transmitter (Fibox 4 trace, PreSens—Precision Sensing GmbH, Regensburg, Germany). Sensor spots (PSt6 and PSt3 for MA and NA samples, respectively) were attached to the packaging film before sealing. Measurements for packages with the CSP labels ($n = 3$) for the first 35 min were performed at room temperature. All other measurements ($n = 4$) were taken in the cooling chamber at 4 ± 1 °C. Initial ambient pressure in the trays was 980 hPa.

2.4. Color measurement

Redness and lightness (CIE values a^* and L^*, respectively) of the ham were measured with a tri-stimulus colorimeter (Chroma Meter CR-410, Konica Minolta Sensing Inc., Osaka, Japan) with illuminant D_{65}, 50 mm aperture size, wide-area illumination/0° viewing angle, 2° standard observer. Per sample, 5 packages were measured and on each package, 3 different locations were measured. Before each measurement the colorimeter was calibrated against a white tile ($Y = 85.4$, $x = 0.3176$, $y = 0.3341$). The samples were measured through the packaging film.

2.5. Statistical analysis

The statistical analysis was performed using R version 3.0.1 (R Foundation for Statistical Computing, Vienna, Austria). A Kruskal–Wallis test with a post-hoc Wilcoxon test was used to assess the differences in discoloration between the samples. A value of $p < 0.01$ was considered to be significant.

3. Results and discussion

3.1. Oxygen scavenging activity of the CSP and changes in oxygen concentration in the headspace

The discoloration of ham is strongly dependent on the headspace oxygen concentration in the package. To measure the effect of different headspace oxygen concentrations on the discoloration of ham and to assess the oxygen scavenging activity of the CSP, ham was packed under modified atmosphere (MA) with 2 vol.% O_2 (with or without CSP) or normal atmosphere (NA) and stored in darkness or illuminated (8 h/day or 24 h/day).

The headspace oxygen concentration of the packages containing the CSP and illuminated 24 h/day decreased rapidly from 2 vol.% to 0.47 vol.% within 2 min (Fig. 1a). Afterwards it further decreased and reached a level of ≤0.05 vol.% after 35 min. Oxygen concentrations remained below 0.05 vol.% during the storage of 21 days (Fig. 1b). As mentioned in previous studies (Larsen et al., 2006; Møller et al., 2003), a packaging with a low oxygen transmission rate is important to prevent diffusion of atmospheric oxygen into the oxygen-free packaging. Previous trials showed an increase in 0.01 vol.% oxygen during 21 days for empty packages as