Meat Science 118 (2016) 8–14

Contents lists available at ScienceDirect

Meat Science

journal homepage: www.elsevier.com/locate/meatsci

Relevance of nanocomposite packaging on the stability of vacuum-packed dry cured ham☆

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ARTICLE INFO

Article history:
Received 9 June 2015
Received in revised form 26 January 2016
Accepted 7 March 2016
Available online 11 March 2016

Keywords:
Clay
Nanocomposite
Polyamide
Skin
TBARS
Vacuum
Meat
Ham

ABSTRACT

In this study effects of a novel high barrier multilayer polyamide film containing dispersed nanoclays (PA_N) on the stability of vacuum packed dry-cured ham were investigated during 90 days refrigerated storage in comparison with non-modified multilayer polyamide (PA) and a commercial high barrier film. Characteristic bands of the mineral in FT-IR spectra confirmed the presence of nanoclays in PA_N, enhancing oxygen transmission barrier properties and UV protection. Packaging in PA_N films did not originate significant changes on colour or lipid oxidation during prolonged storage of vacuum-packed dry-cured ham. Larger oxygen transmission rates in PA films caused changes in CIE b^* during refrigerated storage. Ham quality was not affected by light exposition during 90 days and only curing had a significant benefit on colour and TBARS, being cured samples more stable during storage in all the packages used. Packaging of dry-cured ham in PA_N was equivalent to commercial high barrier films.

1. Introduction

Organically modified layered silicates (organoclays) have been proposed as polymer fillers with promising applications in the food sector. Those materials have high surface areas, and in packaging applications, retain optimal transparency and enhance gas and water vapour barrier properties (Patel, Somani, Bajaj & Jasra, 2009). Barrier properties are improved by an increase in tortuosity obtained by the dispersion of nano-size fillers after delamination of the layered silicates in polymer matrices (Duncan, 2011). At low silicate contents (1–5 wt.%) nanoclay dispersion has also an effect on the physical properties of silicate nanocomposites and the films present improved dimensional stability and thermal resistance. Those mineral clays contribute to the controlled release of bioactive molecules because they have cation exchange capabilities and can be incorporated into biocide surfaces or act as nanosensors (Llorens, Lloret, Picouet, Trbojevich & Fernandez, 2012). The popularity of the nano-clay fillers relies on the inexpensive clays, their high stability, and their multipurpose character. Natural clay platelets are already nanoparticulated, with nanometric thick layers. The organophilic clays are prepared from natural clays by an exchange reaction between hydrophilic clays and an organic cation, such as quaternary ammonia (Picard, Gerard, & Espuche, 2008).

Polyamide-6 (PA6) is an extensively used polymer, highly resistant to abrasion, with excellent elasticity and high tensile strength. PA6 physical and barrier properties can be modified by the incorporation of nanoclays. Enhanced barrier properties to water vapour and oxygen have been described in PA6 nanocomposites by Beatrice, Branciforti, Alves, and Bretas (2010) and Fasihi and Abolghasemi (2011). Picard et al. (2008) reported an improvement in barrier properties of PA6 nanocomposite polymer blends to helium, hydrogen, oxygen, and water. Moreover, the addition of organo-montmorillonite to PA6 produced an increase in viscosity during elongation (Baldi, Franceschini, Bignotti, Tieghi, & Riccò, 2009). Up to now, two studies described positive effects of polyamide nanocomposite blends during MAP packaging for beef loin (Picouet, Fernandez, Realini, & Lloret, 2014) and cooked ham (Lloret, Picouet, Trbojevich, & Fernandez, 2016). Therefore, it is expected that novel PA6 nanocomposite materials could be efficiently implemented in multilayer films with applicability in the food sector, and in particular, in meat packaging products.

Dry-cured ham is a processed meat product highly appreciated by consumers and with high added-value. Typically, pork hams are dry-cured with potassium nitrate or sodium nitrite or a mixture of both. They are kept for prolonged time under refrigeration to inhibit the growth of pathogenic microorganisms and to offer self stable products.

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http://dx.doi.org/10.1016/j.meatsci.2016.03.007
0309-1740/

Table 1
Thickness, oxygen transmission (OTR) and water vapour permeability (WVTR) in PA, PA_N and commercial SK films.

Films	Thickness (μm)	OTR (cm^3/m^2 day bar)	WVTR (g/m^2/day)
PR > F	0.013	<0.0001	0.003
RMSE	3	2	0.043
PA_N	104	44^b	3.0^a
PA	100	96^a	2.2^b
SK	102	2*	7*

* Values following technical data sheet. WVTR (38 °C/90% RH); OTR (23 °C/0% HR). PA_N, multilayer nanocomposite polyamide film; PA, multilayer polyamide film; SK, commercial ultra-high barrier film. Different superscripts indicate significantly different in the same column ($P < 0.05$). RMSE is the root mean square deviation.

The colour in dry-cured meat is due to nitrosylmyoglobin, formed from a reaction between nitrite and myoglobin (Cheftel & Culioli, 1997). However, some special well-appreciated varieties, such as Parma ham, develop a red colour during aging despite the fact that salting was conducted without the addition of nitrate or nitrite (Parolari, Gabba, & Saccani, 2003). In those dried nitrite-free hams, the pigment formed during ageing is zinc-protoporphyrin IX (ZPP), as described by Wakamatsu, Hayashi, Nishimura, and Hattori (2010). After ageing, post-processing operations include deboning, slicing and packaging under vacuum or a modified atmosphere (MAP) without oxygen to minimize the problems associated with oxidation (Cilla, Martínez, Beltran, & Roncales, 2006; Garcia-Esteban, Ansorena, & Astiasaran, 2004; Parra et al., 2010). MAP is more convenient because it prevents samples from sticking but the residual headspace oxygen can affect lipid oxidation (Garcia-Esteban et al., 2004). During commercialisation, dry-cured ham is displayed in refrigerated cabinets under luminance. Thus light and oxygen are the main causes of discoloration, which gradually develops due to the oxidation of the pigments and influences negatively the visual presentation of dry-cured ham.

The main objective of this study was to evaluate the technological potential of novel PA6 nanocomposites. For this, the main morphological attributes of the films were characterized, and the stability of dry-cured and nitrite-free dry-hams, vacuum packed in a PA6 multilayer containing dispersed nanoclays were studied under different illumination conditions during refrigerated storage. As indicators of lipid oxidation and dry-cured ham quality, instrumental colour parameters and TBARS index were recorded during 90 days.

2. Materials and methods

2.1. Fabrication of packaging materials

Two multilayer films have been fabricated with A/B/C structure, with a thickness of approximately 100 μm.

The internal layer C was composed by low-density polyethylene (LDPE Dow 410E); the external layer A was composed of a commercially available nanoclay modified polyamide PA6 (obtained by the courtesy of a private corporation, commercial name not given) or a standard polyamide PA6 (Ultramid B36LN, BASF, Ludwigshafen, Germany). The B layer was a linear low density polyethylene adhesive (Plexar 3236).

The prototype films were obtained by a cast film co-extrusion process at 85 rpm for the LDPE, 18 or 20 rpm for PA or PA_N, and 8 rpm for the adhesive. Two films (160 m long and 300 mm wide) were obtained, one with an external layer composed of standard polyamide called PA and the other one with an external layer of a nanocomposite polyamide called PA_N. The polymer layer thicknesses in microns were LDPE (85 ± 2.5)/PA6 (17 ± 4) or LDPE (91 ± 0.6)/PA_N (12 ± 2.2). An ultra-high-barrier commercial film (skin type, named internally as SK), was used as standard material.

2.2. Characterisation of the films

2.2.1. Ft-IR

The films were characterized using a Perkin-Elmer Spectrum 400. FT-IR/FT-NIR spectrophotometer (Perkin Elmer, Waltham, MA, USA). FT-IR spectra were recorded in the range 400–4500 cm^{-1}. A piece of previously cleaned films was scanned in the transmittance mode.

2.2.2. Colour

CIE L^*, a^* and b^* colour coordinates were measured using a Minolta CR-410 colorimeter (Minolta, Tokyo, Japan) with a D65 illuminant and 2° observation angle. The films were placed on the top of the calibrated white plate ($L_{wp} = 97.71$; $a_{wp} = 0.05$; $b_{wp} = 1.99$) and the colour of a 50 mm area was recorded. Colour changes (ΔE), hue (h^*), chroma (C^*) and white index (*W.I.*) values were calculated using the following equations:

$$\Delta E = \left[(L_{film} - L_{wp})^2 + (a_{film} - a_{wp})^2 + (b_{film} - b_{wp})^2 \right]^{1/2} \quad (1)$$

$$h^* = \text{arctg}\, b_{film}{}^* / a_{film}{}^* \quad (2)$$

$$C^* = (a_{film}{}^{*2} + b_{film}{}^{*2})^{1/2} \quad (3)$$

$$W.I. = 100 - [(100 - L_{film})^2 + (a_{film})^2 + (b_{film})^2]^{1/2} \quad (4)$$

where the subscript *film* indicates the nature of the three different films used (PA_N, PA and SK), and *wp* is for white plate.

2.2.3. Thickness

A micrometer (293–240, Mitutoyo Corporation, Tokyo, Japan) with an accuracy of ± 1 μm was used to measure films thickness. The results were calculated from the average of ten repetitions for each material.

2.2.4. Light transmittance

Film transparency was determined by measuring the light transmittance (in %, Eq. (5)) from 200 to 800 nm using a spectrophotometer (UV-1603, Shimadzu, Kyoto, Japan). Two replicate measures were carried out for each material.

$$T = I/I_0 \times 100 \quad (5)$$

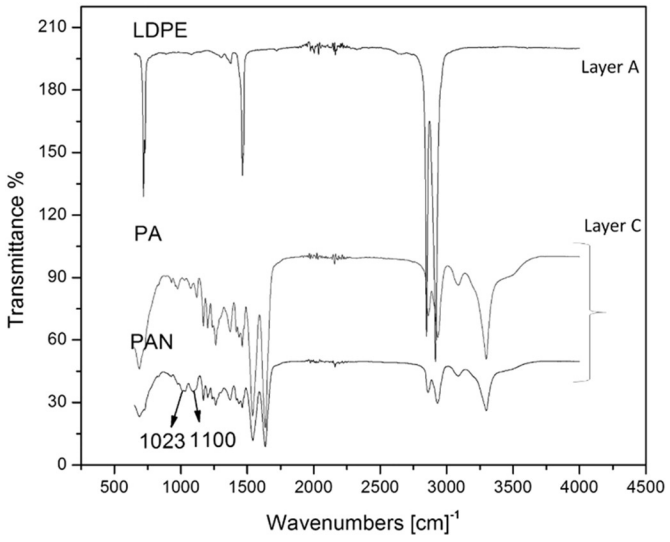

Fig. 1. FTIR spectra of PA (multilayer polyamide) and PA_N (multilayer nanocomposite polyamide) films at the LDPE layer (A) and PA and PA_N layers (B).