LWT - Food Science and Technology 68 (2016) 174–182

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Chemical, sensory, and microbiological stability of stored raw peanuts packaged in polypropylene ventilated bags and high barrier plastic bags

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ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form
12 November 2015
Accepted 14 December 2015
Available online 17 December 2015

Keywords:
peanut
Oxidation
Storage
Quality
Packaging

ABSTRACT

The purpose of this study was to compare the chemical, microbiological, and sensory stability of raw peanuts packaged in high barrier plastic bags (EVOH) under vacuum and in regular polypropylene (PP) ventilated bags during 60 days of storage at 40 °C. The peroxide value showed a higher increase (from 0.38 to 0.95 meqO_2/Kg) in PP samples than in EVOH samples (from 0.38 to 0.63 meqO_2/Kg) during storage. The highest free fatty acids value (0.60g oleic acid/100g peanut oil) was reached by EVOH samples at day 60. The samples packaged in PP pouches showed a significantly higher oleic/linoleic ratio (15.94) and lower iodine value (78.07) with respect to EVOH (13.80 and 80.30, respectively) at the end of storage. A greater decrease of α-tocopherol was observed in PP ventilated bags (from 27.78 to 23.24 mg/100g oil) than in EVOH bags (from 27.78 to 25.10 mg/100g oil). At storage day 60, only molds were detected for both peanut samples but EVOH (2900 CFU/g) showed higher values than PP (2170 CFU/g). An increase of the cardboard flavor and a decrease of roasted peanutty were greater in PP samples. The EVOH bags preserve raw peanuts with better quality in comparison with PP bags.

1. Introduction

The peanut industry's challenge is to preserve chemical, microbiological and sensory quality of peanuts and peanut-containing foods until it reaches the consumer. Lipid oxidation is one of the major causes of peanut deterioration. Oxidative changes affect the overall quality of the end product making it less acceptable or unacceptable for consumers. Those reactions lead to the formation of volatile compounds such as hydrocarbons, alcohols, furans, aldehydes, ketones and acid compounds. Most of these are responsible for off-flavors and certain oxidation compounds are potentially toxic for human health (Akoh & Min, 2002).

Peanut seeds are rich in tocopherols. These are lipid-soluble natural antioxidants that act as free radical scavengers counteracting propagation of the free radical chain so that they protect against lipid oxidation. However, these antioxidants are prone to decomposition, particularly at elevated temperatures and the presence of oxygen molecules resulting in the formation of degradation products, and contributing to sensory or nutritional deterioration (Christopoulos & Tsantili, 2011).

Since oxidative reactions in food lipids are a constant concern for all mentioned above, it is important to know how different factors influence the rate of lipid oxidation to find the best way to keep the oxidative stability in peanuts and by-products during the marketing chain. There are many catalytic factors that can accelerate peanut lipid oxidation in postharvest management. The most important extrinsic factors are storage conditions including temperature, O_2 availability, time, exposure to light and relative humidity (Torres, Barros, Palacios, Chulze, & Battilani, 2014).

An improper handling of storage conditions may also promote the development and colonization of microorganisms. Therefore, in postharvest management, microorganisms continue their multiplication, and if storage conditions are not good, new microorganisms can colonize the product and contribute, along with lipid oxidation, to the emergence of undesirable flavors and mainly affect food safety (Torres et al., 2014).

Food processors attempt to reduce or prevent oxidation and colonization of microorganisms through the application of special

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http://dx.doi.org/10.1016/j.lwt.2015.12.031
0023-6438/

measures to control storage conditions such as the removal of oxygen, addition of antioxidants, use of gas barrier packaging materials, nitrogen-filled headspaces, vacuum packaging and barriers to light (Talcott, 2005). Today, polypropylene (PP) ventilated big bags are the most universally used packaging to transport and store large tons of seeds, particularly peanuts, for long periods of time due to their proven convenience and low cost. However, the effects of this kind of packaging material on lipid oxidation, microbiological contamination and sensory attributes of raw peanuts during certain conditions of storage in comparison to others packaging materials such as ethylene vinyl-alcohol (EVOH) films are unknown. EVOH films are copolymers of ethylene and vinyl alcohol, which have many desirable properties such as their resistance to oils and weather effects, excellent barrier properties with low oxygen and water permeability, ability to prevent insect infestation and contamination with undesirables odors of the surrounding environment (McKeen, 2012).

The purpose of this study was to compare the chemical, microbiological and sensory stability of raw peanuts produced in Argentina, packaged in high barrier plastic bags (EVOH) under vacuum with respect to raw peanuts packaged in regular polypropylene (PP) ventilated bags during storage.

2. Materials and methods

2.1. Materials

Sound and mature seeds of raw peanuts type Runner (cv. Granoleico), size 38/42 kernels per ounce (2013 crop), were provided by the company Lorenzati, Ruetsch & Cia (Ticino, Prov. Córdoba, Argentina).

2.2. Methods

2.2.1. Storage conditions and sampling

Peanut samples (2 kg) were placed in bags (25 cm × 35 cm × 3.6 cm = 3150 cm^3) of two different packaging materials: a) polypropylene (PP) ventilated pouches (Córdoba Envases, Córdoba, Argentina) having 75 μm total thickness and b) high barrier plastic pouches made of ethylene vinyl-alcohol (EVOH) having 175 μm total thickness with an oxygen transmission rate of 1–5 cm^3/m^2/bar/24hs (DISE S.A., Cordoba, Argentina) packaged under vacuum condition (- 760 mmHg) using an industrial packaging machine. In both cases, there was no headspace in the bags because the material used for PP ventilated pouches was holey and the EVOH bags were packed under vacuum. The packaged kernels were placed randomly on shelves and stored in a dark room at 40 °C (accelerated storage conditions) and 60 ± 10% relative humidity for 60 days. The ambient temperature and relative humidity were recorded using a data logger. The samples were removed from storage on day 0, 20, 40, and 60 for analysis.

2.2.2. Peanut kernel moisture content

The moisture was determined by the method 27.500 (AOAC, 2010).

2.2.3. Lipid oxidation indicators

Peanut oil was obtained by cold pressing from the peanut samples using a 20-ton press (HE-DU, Hermes I. Dupraz S.R.L., Córdoba, Argentina). The following indicators were determined on peanut oil samples: peroxide value (PV) expressed as milliequivalents of active oxygen per kilogram of oil, meqO_2/kg (AOAC, 2010); conjugated dienes (CD) and trienes (CT) reported as extinction coefficient E 1%, 1 cm (COI, 2001); and free fatty acids (FFA) expressed as g oleic acid/100 g peanut oil (AOAC, 2010).

2.2.4. Fatty acid composition

The fatty acid methyl esters were analyzed on a Perkin Elmer Clarus 600 gas–liquid chromatograph (Waltham, Massachusetts, USA). A SAC™-5 capillary column (30m × 0.25 mm i.d., 0.25 μm film thickness; C#24156, Supelco) was used. Separation, identification and quantification of the fatty acid methyl esters were performed according to Asensio, Grosso, and Juliani (2015). Iodine value (IV) was calculated from the fatty acid composition using the formula:

$$IV = (\%\,C18:1 \times 0.8601) + (\%\,C18:2 \times 1.7321) + (\%\,C20:1 \times 0.7854)$$

2.2.5. Tocopherol analysis

Tocopherols' concentrations (α, β, γ and δ) in peanut oils were analyzed by HPLC according to Silva, Martinez, Casini, and Grosso (2010) using a Zorbax RX-SIL column (5 μm particle size, 4.6 × 250 mm, Agilent Technologies, Palo Alto, CA, USA). A solution of 0.5% v/v isopropanol in hexane was used as the mobile phase and tocopherols were detected at 298 nm. Identification and quantification of peaks were done by comparing their retention time with those of standards purchased from Sigma–Aldrich (St Louis, MO, USA).

2.2.6. Volatile analysis (VA)

The extraction of volatile compounds of peanut samples was done by solid phase microextraction (HS-SPME) fiber and analyzed by gas chromatography/mass spectrometry (GC/MS) according to Quiroga, Asensio, and Nepote (2014). The SPME fiber used was divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) (Supelco, Bellefonte, PA, USA). Raw peanut seeds (2 g) were ground and placed in a vial at 70 °C for 20 min. The fiber was exposed to the vial headspace for 10 min and then injected into a GC–MS Perkin Elmer Clarus 600 coupled with a mass detector. An ELITE 5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness; Perkin Elmer) was used. The column temperature was programmed from 50 °C (10 min hold) to 280 °C (5 min hold) at a rate of 4 °C/min. Ionization was performed by electron impact at 70 eV. Identification of volatile compounds was performed in full scan mode (m/z 40–550) via a combination of the NIST mass spectral library and gas chromatographic retention times of standard compounds. When standards were not available, volatile compounds were tentatively identified using GC/MS spectra only.

2.2.7. Microbiological count

Counts of aerobic mesophilic bacteria were determined by culturing samples in TSA (Triptone Soya Agar, Britania Lab). Quantitative enumeration was done using the surface-spread method. Ten grams of each milled peanut sample were blended and homogenized in 90 mL peptone water (0.1 g/100 mL) in sterile sample bags. Plates were incubated for 24 h at 37 °C. The results were expressed as colony forming units per g of peanut kernels (CFU/g) (FDA-BAM Online, 2001).

Counting of total yeasts and molds was determined as stated above except that SDA (Sabouraud Dextrose Agar, BritaniaLab) was used as culture medium by pour-plated method. Plates used for counting were those containing 10–100 colony forming units (CFU). All plates were incubated at 25 °C for 5 days (ISO method 7954, 1987).

2.2.8. Sensory descriptive analysis

Peanut samples were roasted at 155 °C for 20 min in an air circulation oven (Garmont, Alta Gracia, Argentina) and blanched

before descriptive analysis (Grosso & Resurreccion, 2002). A trained descriptive sensory panel (9 panelists: 7 women and 2 men) with at least 6 years of experience in evaluating peanut products participated in the analysis. Panelists used a 'hybrid' descriptive analysis method combining the quantitative descriptive analysis (Tragon Corp., Redwood City, CA, USA) and Spectrum TM analysis (Sensory Spectrum, Inc., Chatham, NJ, USA) for evaluating samples (Meilgaard, Civille, & Carr, 2006). A 150 mm unstructured linear scale was used for measuring attribute intensity ratings. All panelists were selected, trained and calibrated according to Grosso and Resurreccion (2002). All samples were evaluated in partitioned booths under fluorescent light at room temperature. A completely randomized block design was used for testing samples. The data were registered on paper ballots.

2.2.9. Statistical analysis

The experiment was run in three repetitions. Data were analyzed using INFOSTAT software Version 2013 (Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Córdoba, Argentina). Two-way analysis of variance (factors: 'treatment' and 'time') and LSD Fisher's multiple range test were developed to figure out significant differences among means in data from chemical and sensory analysis of peanut samples during storage ($\alpha = 0.05$). Pearson coefficients were estimated to stablish correlations between dependent variables. Principal component analysis (PCA) was performed on the correlation matrix of standardized data from chemical and sensory variables. The purpose of the PCA was to explore associations between both treatments, chemical and sensory variables.

3. Results and discussion

3.1. Chemical changes in the samples

Changes in moisture content (MC), peroxide value (PV), conjugated dienes (CD) and trienes (CT) and free fatty acids (FFA) in raw peanut samples packaged in polypropylene ventilated pouches (PP) and high barrier plastic pouches under vacuum (EVOH) are illustrated in Fig. 1. MC decreased significantly between day 0 and 60 for both packaging but this decrease was greater in PP than EVOH, and that remained constant from day 20 (Fig. 1a). The temperature of 40 °C probably caused the samples to lose moisture.

Peroxide value (PV), conjugated dienes (CD) and conjugated trienes (CT) are lipid oxidation indicators used to measure primary oxidative changes. The initial PV, CD, and CT of fresh raw peanuts were very low. These oxidation indicators increased with storage time, and significant differences were found between packaging conditions. With respect to PV, the maximum tolerance value expected in raw peanuts is 2 meq O_2/Kg oil. Both packaging material preserved raw peanuts below this value during storage time. However, PP samples developed higher PV than EVOH samples throughout the storage (Fig. 1b). Similar behavior was observed in the results of CD and CT, as shown in Fig. 1c and d.

Previous researchers (Bakkalbaşı, Yılmaz, Javidipour, & Artık, 2012; Mexis, Badeka, Riganakos, Karakostas, & Kontominas, 2009) reported that the effect of temperature on lipid oxidation was higher than the effect of oxygen permeability and lighting conditions. In the present study, temperature (40 °C) and lighting conditions (dark room) were constants and pre-established; therefore, the changes observed in oxidative indicators between treatments were probably due to differences in packaging conditions. Raw peanuts packaged in EVOH under vacuum exhibited better resistance to lipid oxidation than those packaged in PP ventilated pouches. These results could be explained primarily by the lower permeability to oxygen in EVOH materials with respect to PP ventilated materials. It is also observed that lower loss of moisture occurs in EVOH bags and could also contribute to limit lipid oxidation. The way in which water acts to decrease lipid peroxidation within a given range of increasing water activity was explained by polar bonds that could be established between the polar groups of the lipids and water, so that lipids are taken out of the autoxidation reaction. What is more, water could react with free radicals to form non-radical products and thus facilitate termination reactions (Nelson & Labuza, 1992). Moreover, Abegaz, Kerr, and Koehler (2004) investigated the role of moisture in product flavor and quality changes and demonstrated that the addition of moisture in peanut pastes acts decreasing peroxide value and hexanal contents; therefore, limiting the extent of lipid oxidation in these products.

FFA measurements indicate the degree of glycerid lipolitic decomposition. These reactions occur by lipases (enzymatic hydrolysis) produced in the seeds or by fungi at high temperatures and moisture contents. In this study, FFA increased with storage time for both packaging material. However, EVOH showed significantly higher FFA than PP samples during storage (Fig. 1-e). The highest FFA values reached for raw peanuts packaged in both materials at day 60 were within acceptable limits (lower than 1.00%) (CODEX STAN 200–1995). Other authors (Worang, Dharmaputra, Syarief, & Miftahudin, 2008) found similar increasing tendencies in FFA for nut seeds packed in plastic bags during storage. As fungal population and moisture content decreased during storage, they assumed that lipase activity could be due to seed enzymes. Considering the conclusion of Worang et al. (2008) and the results observed in the present research, the higher formation of FFA in peanuts packaged in EVOH could be related to a greater lipase activity indicating higher seed viability in comparison with those packaged in PP bags. In addition, higher moisture content in samples packaged in EVOH than in PP bags possibly played an important role in the development of enzymatic hydrolytic reactions.

3.2. Fatty acid composition

Fatty acid composition results of raw peanut samples packaged in PP and in EVOH under vacuum during storage are summarized in Table 1. The major fatty acids found in peanut samples were oleic acid followed by linoleic and palmitic acids. O/L and S/U ratios increased significantly during storage time until day 40 for PP samples. In EVOH samples, there were significant differences only at day 60 with respect to day 0 for both ratios. On the other hand, IV decreased with storage time for PP since for EVOH samples, there were no significant differences until day 40 and between 40 and 60 days. PP samples showed, in general, a greater decrease in unsaturated fatty acids (oleic, linoleic, and eicosenoic acids) during storage time in comparison to EVOH samples, resulting in an increase of saturated fatty acids (palmitic, stearic, arachidic, behenic, and lignoceric acids). This behavior was observed in the fatty acids, and could be explained by the fact that double bonds of unsaturated fatty acids are more susceptible to oxidation reactions. Mexis, Badeka, & Kontominas (2009) investigated the effect of active and modified atmosphere packaging, container oxygen barrier and storage conditions on fatty acid composition of raw ground almonds. They concluded that the use of a barrier packaging material and oxygen absorber were the optimum conditions for packaging and storage of raw almonds. In the present research, EVOH pouches preserved the fatty acids profile of the fresh product for a longer time with respect to PP ventilated pouches.

3.3. Tocopherol contents

Tocopherol contents of peanut samples are shown in Table 2.

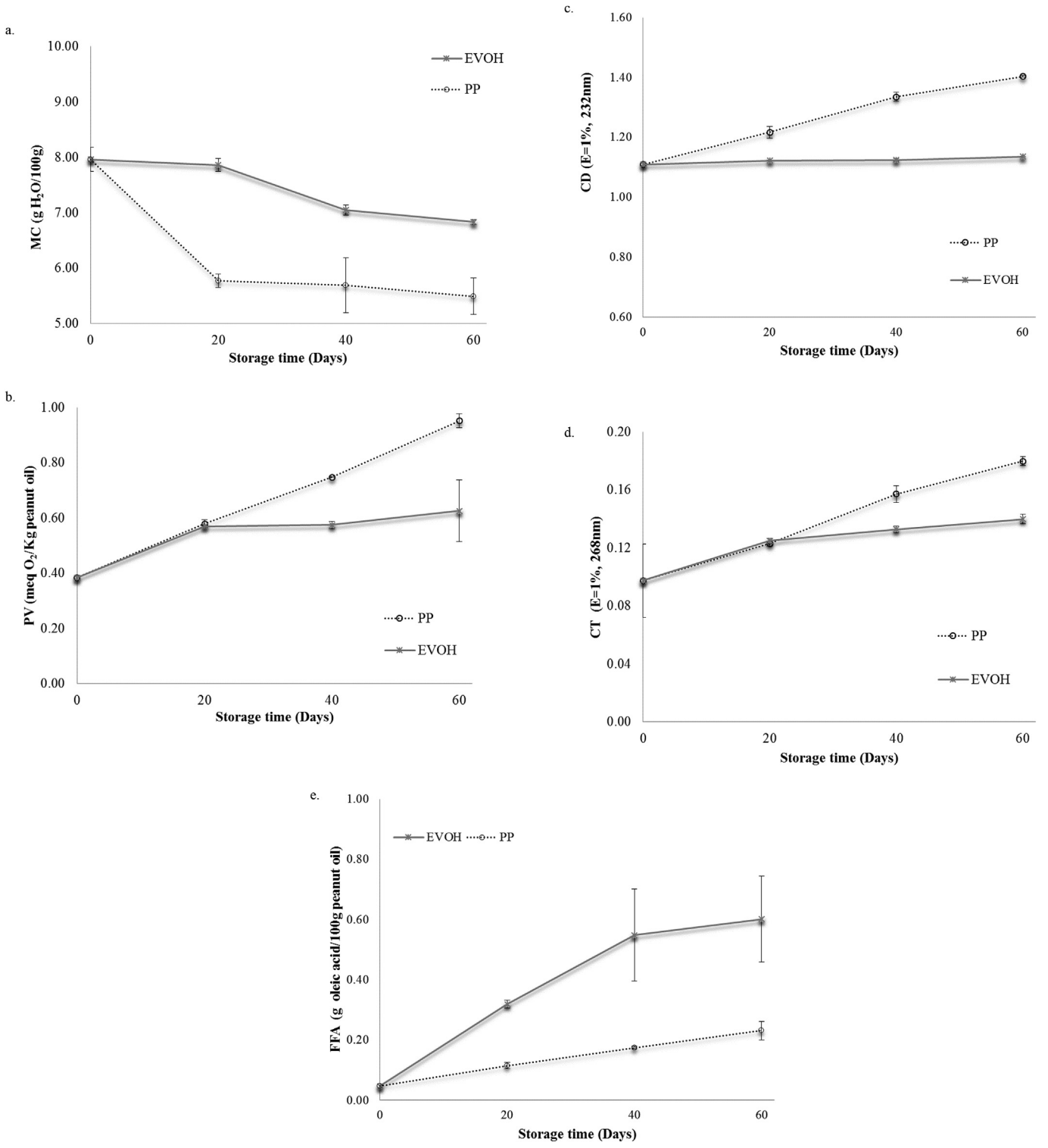

Fig. 1. (a) Peanut kernel moisture content (MC), (b) Peroxide value (PV), (c) Conjugated dienes (CD), (d) Conjugated trienes (CT) and (e) Free fatty acids (FFA) in raw peanuts packaged in polypropylene ventilated pouches (PP) and high barrier plastic pouches (EVOH) under vacuum analyzed during storage at 40 °C and 60 ± 10% relative humidity (n = 3).

Over 55% of the total tocopherols present at day 0 were in the form of α-tocopherol. The next most abundant tocopherol in the samples was γ-tocopherol. The other tocopherols (β and δ-tocopherols) showed very low concentrations. Shin, Pegg, Phillips, and Eitenmiller (2010) also found that α and γ-tocopherol were in a higher concentration than β and δ-tocopherol for high oleic peanuts from the USA.

In this study it was observed that the content of all tocopherols decreased with storage time. The α and γ-tocopherols decreased significantly with storage time from day 0 to day 60 for both treatments, but the decrease observed for samples packaged in PP ventilated bags was higher than the produced in samples packaged

Table 1
Fatty acid composition of raw peanuts packaged in polypropylene ventilated pouches (PP) and high barrier plastic pouches (EVOH) under vacuum analyzed during storage at 40 °C and 60 ± 10% relative humidity.

Fatty acids	Composition (g/100g fatty acids)						
	Day 0[a]	PP[a]			EVOH[a]		
		20 days	40 days	60 days	20 days	40 days	60 days
Palmitic acid (C16:0)	5.37 ± 0.03a	5.49 ± 0.04c	5.70 ± 0.04d	5.77 ± 0.06d	5.38 ± 0.03 ab	5.45 ± 0.06bc	5.48 ± 0.05c
Heptadecanoic acid (C17:0)	TRACES						
Stearic acid (C18:0)	1.49 ± 0.05a	1.58 ± 0.12abc	1.70 ± 0.11cd	1.77 ± 0.07d	1.52 ± 0.03 ab	1.58 ± 0.02abc	1.63 ± 0.04bc
Oleic acid (C18:1)	79.48 ± 0.06d	79.29 ± 0.01c	79.11 ± 0.04b	78.64 ± 0.05a	79.44 ± 0.05d	79.35 ± 0.07c	79.28 ± 0.03c
Linoleic acid (C18:2)	6.05 ± 0.14e	5.61 ± 0.15c	5.21 ± 0.30b	4.94 ± 0.07a	6.00 ± 0.06de	5.83 ± 0.12cde	5.75 ± 0.05cd
Arachidic acid (C20:0)	0.71 ± 0.09a	0.86 ± 0.11 ab	1.07 ± 0.06b	1.09 ± 0.11b	0.84 ± 0.06a	0.85 ± 0.05a	0.68 ± 0.10a
Eicosenoic acid (C20:1)	2.74 ± 0.02d	2.63 ± 0.03c	2.53 ± 0.03b	2.37 ± 0.07a	2.75 ± 0.06d	2.69 ± 0.01cd	2.72 ± 0.03d
Behenic acid (C22:0)	2.26 ± 0.04a	2.30 ± 0.10a	2.32 ± 0.01a	2.72 ± 0.06b	2.35 ± 0.15a	2.40 ± 0.07a	2.43 ± 0.21a
Erucic Acid (C22:1)	0.22 ± 0.04a	0.25 ± 0.05a	0.25 ± 0.01a	0.31 ± 0.04a	0.30 ± 0.01a	0.22 ± 0.05a	0.18 ± 0.02a
Lignoceric acid (C24:0)	1.56 ± 0.04a	1.66 ± 0.04a	1.81 ± 0.06b	2.11 ± 0.14c	1.59 ± 0.05a	1.61 ± 0.07a	1.88 ± 0.06b
Oleic/linoleic ratio	13.14 ± 0.30c	13.94 ± 0.21b	15.21 ± 0.82a	15.94 ± 0.31a	13.23 ± 0.15c	13.61 ± 0.29bc	13.80 ± 0.13b
Saturated/unsaturated ratio	0.13 ± 0.00c	0.14 ± 0.00b	0.14 ± 0.00b	0.15 ± 0.00a	0.13 ± 0.00c	0.14 ± 0.00bc	0.14 ± 0.00b
Iodine value	81.00 ± 0.31a	80.11 ± 0.15b	79.05 ± 0.52c	78.07 ± 0.06d	80.85 ± 0.02a	80.55 ± 0.00 ab	80.30 ± 0.07b

[a] Means ± standard deviation followed by different letters in each row indicate significant differences at $\alpha = 0.05$ (n = 3, LSD Fisher).

Table 2
Tocopherol content of raw peanuts packaged in polypropylene ventilated pouches (PP) and high barrier plastic pouches (EVOH) under vacuum, during storage time at 40 °C and 60 ± 10% relative humidity.

Tocopherol	Tocopherol content (mg/100g peanut oil)						
	Day 0[a]	PP[a]			EVOH[a]		
		20 days	40 days	60 days	20 days	40 days	60 days
α-tocopherol	27.78 ± 0.37e	25.08 ± 0.60bc	24.19 ± 0.80 ab	23.24 ± 0.37a	26.49 ± 0.19d	25.71 ± 0.81cd	25.10 ± 0.64bc
β-tocopherol	0.95 ± 0.05b	0.76 ± 0.07a	0.74 ± 0.02a	0.72 ± 0.01a	0.82 ± 0.02a	0.79 ± 0.01a	0.75 ± 0.07a
γ-tocopherol	22.00 ± 0.07e	21.41 ± 0.01c	21.19 ± 0.03b	21.01 ± 0.06a	21.88 ± 0.03de	21.78 ± 0.09d	21.54 ± 0.12c
δ-tocopherol	0.66 ± 0.02b	0.53 ± 0.01a	0.52 ± 0.01a	0.51 ± 0.00a	0.65 ± 0.00b	0.53 ± 0.00a	0.52 ± 0.01a

[a] Means ± standard deviation followed by different letters in each row indicate significant differences at $\alpha = 0.05$ (n = 3, LSD Fisher).

in EVOH bags. The β-tocopherol only showed significant differences for day 0 and 20 for both treatments, but from day 20 it remained constant without significant differences between samples. The δ-tocopherol decreased with storage time but EVOH samples did not show a significant decrease until day 40, remaining constant on day 60, while for PP samples, significant differences appeared from day 20 and remaining constant from then on. The α-tocopherol presented the greatest deterioration during storage time for both treatments. These results are consistent with those reported by Silva et al. (2010) who studied tocopherol contents in stored roasted peanuts. They found that α-tocopherol was more sensitive to deterioration than the other tocopherols.

The degradation of tocopherols are influenced by the same factors that oxidize unsaturated lipids (Roman, Heyd, Broyart, Castillo, & Maillard, 2013). In this study, all tocopherols had a higher rate of degradation throughout storage in peanut samples packaged in PP pouches than in samples packaged in EVOH pouches. A better preservation of tocopherols in raw peanuts samples packaged in EVOH bags allows them to keep a higher antioxidant activity with respect to peanuts packaged in PP bags, resulting in a significantly lower production of oxidation markers.

3.4. Volatile compounds

Table 3 summarizes volatile organic compounds identified in raw peanut samples during storage. Only three relevant peaks were found at storage day 0. Cyclobutanol was also found in others raw peanut samples by (Burroni, Grosso, & Guzmán, 1997). In contrast, they detected trace amounts in roasted and fried peanut samples. These results could indicate that cyclobutanol would be a marker of a fresh product, which is susceptible to degradation throughout storage. Ara, Shinwari, Rashed, and Bakir (2013) reported high percentages of cyclobutanol (91.70%) and cyclopropyl carbinol (84.50%) in two extracts from walnuts, and concluded that these compounds were responsible for the strong antimicrobial activity of these samples. In the present study, cyclobutanol was only detected at storage day 0. In the case of cyclopropyl carbinol, it was not detected at day 20, 40, and 60 for PP samples. On the other hand, this volatile compound appeared along with storage time in EVOH, showing a significant decrease until day 40 and was not detected at day 60.

Decane,5,6-bis(2,2-dimethylpropylidene)-,(E,Z)- was found during the storage period but showed a decrease from day 0 to day 60, significantly more pronounced in PP samples than in EVOH samples. Other authors (Haroun, Elghamry, Abdel-Shakour, Elmorsy, & Zahem, 2014) found that decane,5,6-bis(2,2-dimethylpropylidene)-,(E,Z)- was part of the bioactive compounds of a plant extract (Artemizia herba alba) known by its antimicrobial effects against some bacteria species. Similar results were reported by, Nahar, Shahedur Rahman, Mizanur Rahman, and Moniruzzaman (2016) in the essential oil of a legume (Trigonella foenum-graecum) that belongs to the same family plant (Fabaceae) of peanuts. In the present study, the results revealed that cyclopropyl carbinol and decane,5,6-bis(2,2-dimethylpropylidene)-,(E,Z)- had similar tendencies to cyclobutanol in peanut samples. They decreased during storage time, with a higher rate in PP samples. These compounds could be used as markers of fresh raw peanuts. In other studies in peanuts, Pizzolitto et al. (2013) reported that others natural compounds (probably catechin, epicatechin, protocatechuic, caffeic and ferulic acids, and resveratrol) found in peanut skins inhibite fungal growth and fumonisin production.

Ory, Crippen, and Lovegren (1992) reported that in samples

Table 3
Volatile compounds (electronic counts. 10^3) per gram of raw peanuts packaged in polypropylene ventilated pouches (PP) and in high barrier plastic pouches (EVOH) under vacuum analyzed during storage at 40 °C and 60 ± 10% relative humidity.

Volatile compound	Day 0[a]	PP[a]			EVOH[a]		
		20 days	40 days	60 days	20 days	40 days	60 days
Alcohols							
Cyclobutanol	69 ± 1.55	ND	ND	ND	ND	ND	ND
Cyclopropyl carbinol	18 ± 0.23a	ND	ND	ND	17 ± 0.11b	14 ± 0.18c	ND
Alkanes							
Undecane	ND	22 ± 0.72c	28 ± 1.46b	43 ± 0.41a	21 ± 0.77c	26 ± 1.54b	28 ± 2.26b
Dodecane	ND	60 ± 2.02c	219 ± 6.99 ab	237 ± 23.22a	51 ± 0.59c	61 ± 1.33c	213 ± 15.79b
Tridecane	ND	51 ± 3.09bc	54 ± 4.56b	63 ± 5.42a	46 ± 0.29c	52 ± 4.13bc	53 ± 4.46b
Tetradecane	ND	74 ± 3.08d	2564 ± 27.40b	2753 ± 21.10a	53 ± 1.29d	55 ± 3.11d	1870 ± 23.95c
Pentadecane	ND	50 ± 1.00e	103 ± 3.18b	107 ± 0.28a	53 ± 1.35d	54 ± 1.51d	72 ± 2.74c
Hexadecane	ND	33 ± 0.96d	2115 ± 9.36b	2189 ± 4.27a	24 ± 0.48d	30 ± 1.59d	1254 ± 36.51c
Octadecane	ND	12 ± 0.80e	495 ± 3.11b	535 ± 4.56a	ND	18 ± 0.49d	270 ± 2.85c
Nonadecane	ND	15 ± 0.96d	52 ± 0.47b	56 ± 0.44a	ND	13 ± 0.65e	41 ± 0.75c
Decane,5,6-bis(2,2-dimethylpropylidene)-,(E,Z)-	670 ± 33.42a	623 ± 24.63bc	620 ± 21.31bc	381 ± 18.16d	626 ± 16.16b	611 ± 19.29bc	578 ± 14.41c

ND = Not detected.
[a] Means ± standard deviation followed by different letters in each row indicate significant differences at $\alpha = 0.05$ (n = 3, LSD Fisher).

stored under no ideal conditions, another type of lipid oxidation molecules appeared in the form of a homologous series of hydrocarbons. These hydrocarbons seem to affect flavor or could indicate future flavor problems. From day 20 to day 60 for both peanut samples in the present investigation, new peaks appeared and eight of them were identified as saturated hydrocarbons forming the homologous series. Undecane to hexadecane homologous series of saturated hydrocarbons appeared in both samples and showed a higher increase in PP samples than in EVOH samples. Heptadecane could not be identified. Octadecane and nonadecane appeared in PP samples at day 20, 40, and 60 but only at day 40 and 60 for EVOH samples.

The homologous series of hydrocarbons appeared in the studied storage conditions. However, EVOH bags under vacuum preserved the raw peanuts with a better volatile profile quality than PP samples.

3.5. Microbiological counts

Microbial contamination in stored peanuts should be controlled for the safety and quality of the product. *Aspergillus flavus* and *Aspergillus parasiticus* are the most frequent mold species responsible for the colonization and contamination of stored peanuts, being the most important producers of aflatoxins (Torres et al., 2014).

All samples were evaluated at day 0 and 60 to detect levels of total aerobic mesophilic bacteria, yeasts and molds. At day 0, less than 10 CFU/g aerobic mesophilic bacteria, yeasts and molds were detected. At storage day 60, only molds were detected for both peanut samples but EVOH (2900 CFU/g) showed higher values than PP (2170 CFU/g). Most fungi are obligate aerobes and require oxygen to live. Although peanuts stored in EVOH pouches had the microenvironment modified by vacuum, low levels of oxygen were able to stay inside the bag. This situation, combined with the higher moisture content in EVOH samples in comparison to PP samples during storage, probably encouraged molds to grow in the former. However, there was no visible mold growth in either peanut sample.

There are no specific limits for total yeasts and molds counts in raw peanuts due to the fact that these products must be roasted before consuming which contributes to kill many microorganisms. Nevertheless, owing to the association between aflatoxins-molds with toxicity and carcinogenicity in humans and animals, it is of global concern to reduce the risk of its occurrence in peanuts and derivate. It is well stablished that one of the most important factors that contributes to contamination of stored peanuts is the high moisture content (Zorzete et al., 2013). Aflatoxin production is generally correlated with kernel moisture contents of 10 g H_2O/100g or higher. The range of moisture content found in the present research (day 0 = 7.96 g H_2O/100g, day 60 = 6.83 g H_2O/100g) is considered as safe for stored peanuts (Torres et al., 2014).

3.6. Sensory descriptive analysis

Mean intensity ratings (scale 0–150 mm) of the sensory attributes obtained from descriptive analysis at day zero (fresh product) were: brown color = 49.33 ± 0.26, roughness = 11.83 ± 0.38, glossiness = 10.21 ± 0.07, roasted peanutty = 81.71 ± 0.07, oxidized = 0, cardboard = 8.25 ± 0.22, sweetness = 20.71 ± 0.07, saltiness = 5.29 ± 0.07, sourness = 5.12 ± 0.13, bitterness = 6.33 ± 0.19, astringent = 18.12 ± 0.00, hardness = 43.87 ± 0.22 and crunchiness = 42.54 ± 0.19. Similar intensity rating attributes were reported by Grosso and Resurreccion (2002).

The sensory attributes that changed during storage time were cardboard and roasted peanutty. The intensity ratings of cardboard and roasted peanutty flavors at storage days 0, 20, 40, and 60 for EVOH and PP samples are presented in Fig. 2. The cardboard intensity ratings of this attribute increased with storage time ($p < 0.0001$). This trend was also found in earlier investigations (Quiroga et al., 2014; Riveros, Mestrallet, Quiroga, Nepote, & Grosso, 2013). There were no significant differences between the packaging materials until storage day 40 when PP samples showed higher intensity ratings than EVOH samples. Since cardboard is an attribute related to the lipids oxidation, these results could indicate that EVOH packaging under vacuum could retard lipid oxidation of raw peanuts, while lipid deterioration reactions continued in PP pouches as observed in chemical indicators. These results are comparable to the findings reported by Bakkalbaşı et al. (2012) who studied the effect of packaging materials, storage conditions, and variety on the oxidative stability of walnuts. Those authors concluded that the use of a packaging material with low oxygen permeability under vacuum leads to the inhibition of lipid peroxidation and increased shelf-life of walnuts for up to 12 months.

Roasted peanutty flavor is the attribute used to characterize typical roasted peanut flavor in peanut products; and is related to certain molecules like alquilpyrazines which are produced in the roasting process as a consequence of the reactions between the

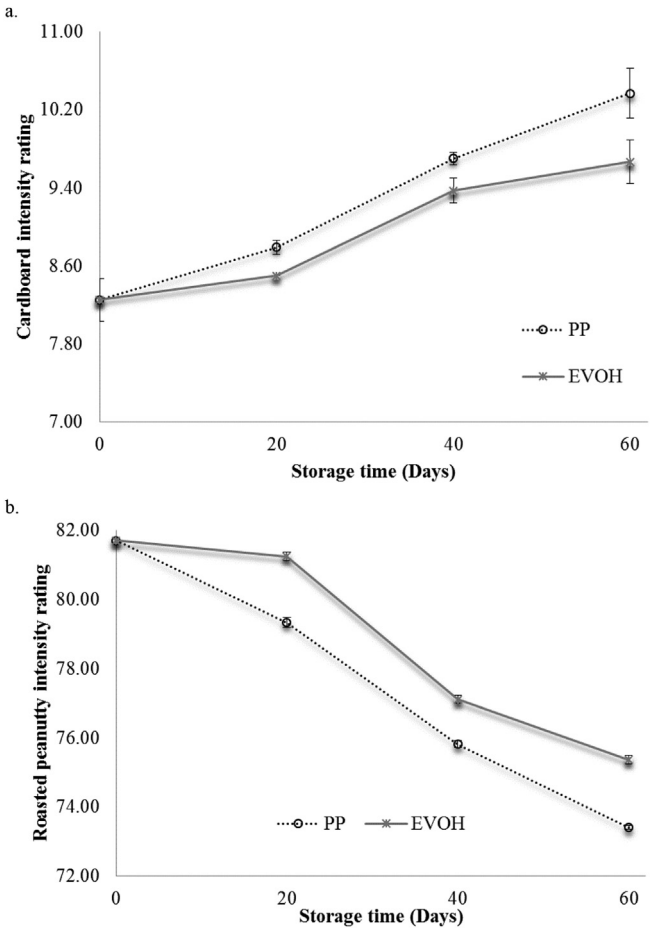

Fig. 2. Intensity ratings of sensory attributes: (a) cardboard and (b) roasted peanutty in raw peanuts packaged in high barrier plastic pouches (EVOH) under vacuum and polypropylene ventilated pouches (PP) evaluated during storage at 40 °C and 60 ± 10% relative humidity (n = 3).

amine groups of proteins with carbohydrates (Grosso & Resurreccion, 2002). In this study, roasted peanutty flavor decreased with storage time ($p < 0.0001$). This decrease was higher in PP samples than in EVOH samples. It was reported that a decrease in this sensory attribute is correlated with a decrease in the alquilpyrazine content (Bett & Boylston, 1992). Since in this study, raw peanuts were roasted at the moment of the sensory analysis, the results could indicate degradation in aminoacids and sugars during storage time, so during the roasting process there was a decline in the formation of alquilpyrazines with the subsequent decrease in roasted peanutty flavor. As a consequence, higher scores for roasted peanutty flavor observed in EVOH samples in comparison to PP ones throughout storage possibly indicate a lower deterioration rate of proteins and carbohydrates in the former.

As mentioned above, the moisture content in a food product could have an important effect on flavor changes due to the protective properties of water against oxidation process (Nelson & Labuza, 1992). In addition, Reed, Sims, Gorbet and O'Keefe (2002) reported that the highest water activity treatments in roasted high oleic peanuts (HOP) produce fewer off-flavor compounds with lower off-flavor notes in comparison to HOP with the lowest water activity. In the present research, higher moisture content and lower oxidation rates during storage of raw peanuts packaged in EVOH under vacuum in comparison with raw peanuts stored in PP ventilated pouches allowed the former to preserve flavor stability in a more efficient way.

3.7. Principal component analysis

A principal component analysis (PCA) was conducted in order to compare both packaging materials (PP or EVOH) with respect to their ability to preserve oxidative stability and sensory quality of raw peanut kernels during storage. The biplot obtained from the first two principal components (PC) in the PCA is presented in Fig. 3. The first two PCs explained 90.2% variability in the samples during 60 days of storage. The variables MC, IV, tocopherol contents (α, β, γ, and δ-tocopherols), volatiles related to fresh product cyclobutanol, cyclopropyl carbinol, decane,5,6-bis(2,2-dimethylpropylidene)-,(E,Z)-, and roasted peanutty flavor were placed on the right side (PC1) of the biplot. These variables showed positive association between them; but they were negatively related to chemical oxidative indicators (PV, CD, and CT), S/U ratio, O/L ratio, cardboard, some of the volatiles considered indicators of future flavor problems (undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, octadecane, and nonadecane), and FFA (although, it showed poor association mainly with O/L, S/U and IV). Therefore, peanut samples with lower values for the variables related to lipid oxidation appeared to the right side, and peanut samples with higher results for these variables were placed on the left side (negatives values in CP1) of the biplot. Most of these associations were confirmed by correlation analysis (Pearson coefficients). PP and EVOH samples at day 0 were placed more to the right followed by EVOH samples at day 20. In contrast, PP samples at day 40 and 60 appeared more to the left.

There are quality attributes, such as flavor, nutritive value, safety, and overall quality that must be preserved to ensure the stability and acceptability of peanuts. Peanut spoilage begins trough primary oxidative reactions followed by secondary pathways, which lead to the development of rancidity and off-flavors; degradation of lipids, proteins, and tocopherols; and occurrence of toxic substances. In the present research, the lipid oxidation indicators (PV, CD, and CT) were used to follow the primary oxidative reactions in the peanut samples. They increased with storage time but they exhibited significant higher values in PP than in EVOH. Initial oxidative products broke down during storage giving rise to the formation of decomposition products such as the volatiles considered indicator of future flavor problems (undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, octadecane, and nonadecane) which appeared in greater amount in PP than in EVOH. Higher rate of deterioration observed in PP than in EVOH also led to a greater degradation of fatty acids and tocopherols in the former due to these molecules are prone to oxidation. For that reason, PP bags were positively associated with S/U and O/L ratios, and negatively associated with IV and tocopherols contents. Moreover, the occurrence of certain undesirable molecules like it is mentioned above could be responsible for higher rating of cardboard flavor observed in PP bags. These facts indicate that raw peanuts stored in PP bags showed a greater tendency to oxidative deterioration and loss of sensory quality than raw peanuts stored in EVOH bags.

In addition, correlation coefficients higher than 0.65 were observed among PV, CD, CT, FFA, cardboard flavor and O/L ratio. Negative correlation coefficients higher than −0.65 were observed between MC, roasted peanutty flavor, IV, α-tocopherol and the variables mentioned above for both samples. These results were due to the fact that MC, roasted peanutty flavor, IV, and α-tocopherol decreased while PV, CD, CT, FFAs, cardboard and O/L increased with storage. In previous works, relations between chemical and sensory variables were reported for other products (Bakkalbaşı et al. 2012; Olmedo, Nepote, & Grosso, 2013).

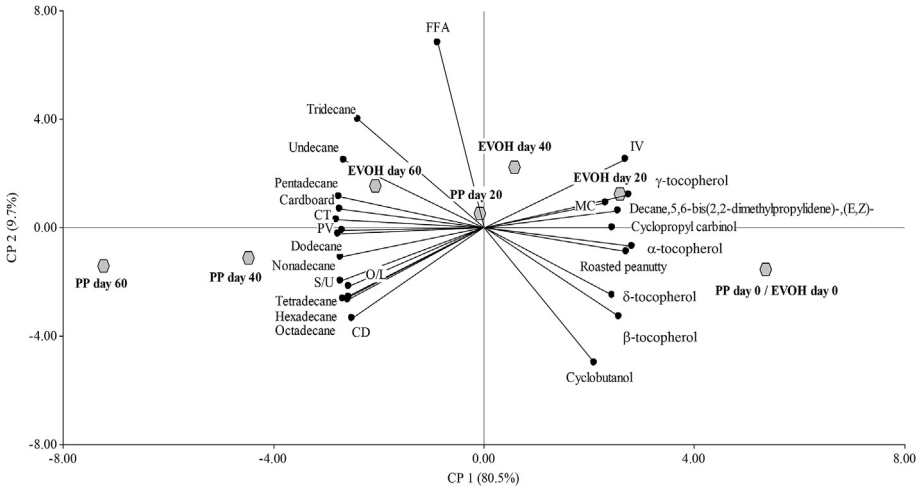

Fig. 3. Biplot from the first and second components from principal component analysis. Variables: peroxide value (PV), conjugated dienes and trienes (CD and CT), free fatty acids (FFA), moisture content (MC), saturated/unsaturated fatty acids ratio (S/U), oleic/linoleic ratio (O/L), iodine value (IV), tocopherols (α, β, γ and δ), cardboard and roasted peanutty flavors, and volatile compounds like cyclobutanol, cyclopropyl carbinol, decane,5,6-bis(2,2-dimethylpropylidene)-,(E,Z), undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, octadecane, and nonadecane. Treatments: raw peanuts packaged in high barrier plastic pouches (EVOH) under vacuum and raw peanuts packaged in polypropylene ventilated pouches (PP) evaluated at storage days 0, 20, 40, and 60 under storage condition of 40 °C and 60 ± 10% relative humidity (n = 3).

Finally as additional comment related to the packaging cost, the estimative price of EVOH bag material (U$S35/1000 kg bag) is higher than PP bag material (U$S12/1000 kg bag) but raw peanuts packaged in EVOH bags will preserve better chemical and sensory quality parameters during storage increasing their shelf-life. In addition, raw peanuts packaged in EVOH bags will not have problem with insect infestation and humidity interchange with relative humidity from the environment which will help to save money avoiding fumigation and decreasing energy expenditure for cold storage.

4. Conclusions

High barrier plastic bags (EVOH) provide raw peanuts with a higher protective effect against deterioration of the chemical parameters and sensory quality in comparison to regular polypropylene (PP) ventilated materials during storage time. The findings reported in this study also show that raw peanuts packaged in EVOH under vacuum preserve in a suitable way the microbiological quality during storage. Only, the free fatty acids considered a negative parameter for raw peanuts is the variable that increases in higher proportion in raw peanut samples packaged in EVOH at the beginning of storage in comparison with samples packaged in PP.

Even though, PP bags are actually the most common packaging systems to transport and store peanuts due to their low costs, the peanut industry should consider to replace these types of packaging for EVOH materials under vacuum as a cost-effective alternative. The EVOH bags extend the shelf-life of raw peanuts preserving in better conditions chemical, microbiological, and sensory properties of these products. In addition, this packaging material is a solid and effective barrier between the product and the external environment which, in turn, prevents insects' infestation, growth and development.

Acknowledgments

This research was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PIP # 11220120100371CO) and Secretaría de Ciencia y Tecnología (SECYT-UNC, # 203/14).

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