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# Extension of shelf life of two fatty foods using a new antioxidant multilayer packaging containing green tea extract

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ABSTRACT

The performance of an antioxidant multilayer packaging containing green tea extract was studied over a long-term experiment with real commercial food. Two types of food (dark chocolate peanuts and milk chocolate cereals) were packaged and tested during 16 months. Antioxidant performance of the multilayer packaging was demonstrated. Volatile profile (hexanal, pyrazines and related compounds) and fatty acids were used as indicators to monitor the system performance. The volatile compounds wereanalyzed monthly, identified and quantified by HS-SPME-GC-MS, while the fatty acids were analyzed after derivatization by GC-MS every 3 months. Significant lower values of hexanal were obtained for the active system during the time experiment while the values for the fatty acids were higher in the active system compared to the non-active one. Organoleptic tests carried out with a trained panel confirmed the antioxidant effect. The radical scavenger capacity of the multilayer was also quantitatively evaluated. The new approach of antioxidant behavior as a radical scavenger of green tea is discussed in detail.

*Industrial relevance:* This paper describes the performance of a new antioxidant multilayer packaging material, tested for 16 months with real food and in industrial conditions, as the format, size and material were produced at an industrial level, as a new prototype, following the indications from previous research. In this material green tea extract has been grafted in the internal layer of a multilayer material, in which it acts as a radical scavenger, which means as an antioxidant. The antioxidant behavior of the polymer as well as the performance of the polymer versus real food is described. It is the first time that such a material is successfully produced at the industrial level and in fact, the material is nowadays in the market. For all these reasons the paper is of great industrial relevance. Many industries are and will be interested in it.



## 1. Introduction

Food oxidation is considered a major cause of quality deterioration, affecting both the nutritional and sensory quality and safety of foods and has thus been a challenge for food preservation. Peanuts and cereals covered by chocolate are dried foods that are susceptible to lipid autoxidation due to a high content of unsaturated fatty acids. Flavor and quality of peanuts and peanut products are largely functions of lipid chemistry. Peanuts contain ~50% oil (Cobb & Johnson, 1973). Palmitic acid (16:0), oleic acid (18:1), and linoleic acid (18:2) are the major fatty acids in peanuts and may comprise >90% of the total fatty acids (Ahmed & Young, 1982). The remaining fatty acids, stearic (18:0), arachidic (20:0), eicosenoic (20:1), behenic (22:0), and lignoceric (24:0) acid, normally occur in weight percentages between 0.02 and 4.0%. Free radicals are important chain-carrying intermediates in lipid autoxidation, which lead to the formation of hydroperoxides, which are further precursors of secondary oxidation products, such as ketones and aldehydes. This process may be accelerated by moisture, light, oxygen or exposure to high temperatures. The presence of secondary oxidation products (i.e., aldehydes) is associated with changes inodor and flavor of the products, resulting in rancidity. Hexanal is formed during the oxidation of linoleic acid via the 13-hydroperoxide and it has an odor described as "grassy" which contributes to off-flavors. It is easily detected as it has a low odor threshold (in water: 4.5 μg/kg) (Fenaille, Visani, Fumeaux, Milo, & Guy, 2003, Ruiz, Ventanas, & Cava, 2001). Measurements of hexanal and other secondary oxidation products (e.g., pentanal or octanal) using headspace solid phase microextraction coupled to gas chromatography mass spectrometry (HS-SPME-GC-MS) has been widely used to monitor the oxidative deterioration of dry foods (e.g., peanuts, potato chips) (Sanches-Silva, Rodríguez-Bernaldo de Quirós, López-Hernandez, & Paseiro-Losada, 2004). Flavor compounds produced from roasting peanuts are very important for acceptability. The most important compounds produced after roasting the peanuts or cereals are pyrazines (Ho, Jim, Lee, & Chang, 1961). Loss of peanut flavor occurs rapidly after roasting and is known as flavor fade (Reed, Sims, Gorbet, & O'Keefe,

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2002). Auto-oxidation is a slow, radical process that can take several days (Ingold, 1961).

Active compounds and ingredients can be incorporated into packaging materials to provide several functions that do not exist in conventional packaging systems. Active packaging may carry antioxidants, antimicrobial agents and/or nutrients. Due to health concerns of consumers and environmental problems, current research in this type of packaging has been focused on the use of natural components and biodegradable packaging materials (Suppakul, Miltz, Sonneveld, & Bigger, 2003, López, Sánchez, Batlle, & Nerín, 2007, Gutiérrez, Sánchez, Batlle, López, & Nerín, 2009, Rodríguez-Lafuente, Batlle, & Nerín, 2010, Nerín et al., 2006). Substances with antioxidant potential are available from a variety of natural sources or as synthetic chemicals. Among them green tea extract (GTE) can be mentioned as a rich source of polyphenol antioxidants, particularly catechins (Colón & Nerín, 2012) and has the status of food additive (Roy et al., 2010; Fernandez, Martin, Gonzalez, & Pablos, 2000). A formula for antioxidant packaging based on GTE for food packaging applications was developed in a recent publication by Carrizo, Gullo, Bosetti, and Nerín (2014). In this paper a multilayer antioxidant packaging material has been developed and evaluated first in vitro and later in vivo for its antioxidant properties. The new packaging material was initially produced at laboratory scale and later at industrial scale.

One of the main difficulties when developing an antioxidant material for food protection is the incorporation of the active agent in an efficient and feasible way, so that the new material can act as an antioxidant without modifying the packaging line or the characteristics of the packaged product. Several approaches have been proposed but all of them fail by one or another reason. Extrusion of polymers involves high temperature and the active agents decompose. Coating systems affect the sensory properties of the packaged food when essential oils are used as antioxidants. However, in all these approaches the antioxidant agent is incorporated in the layer in contact with food. In the present work a very different system has been explored. To understand the antioxidant performance in this case a clear idea of the oxidation reaction of lipids is essential. It is known that the oxidation process is a radical reaction initiated by the presence of OH and O free radicals (Nerín, 2011). It is a chain reaction including initiation, propagation and termination. When free radicals are removed the reaction does not take place. If the free radicals can efficiently diffuse through the polymer it is not necessary that the active agent, GTE in this case, were in the layer in contact with the food. This is the principle applied to this new active material.

The aim of this work was to evaluate the performance of a new active multilayer packaging material, based on GTE and produced at industrial scale, in two commercial foods during a long-term experiment (16 months) as well as to demonstrate the efficiency of the new antioxidant material in extending the shelf life of real food.

## 2. Materials & methods

Dark chocolate roasted peanuts and milk chocolate cereals were produced by CHOCOLATES LACASA S.A (Zaragoza, Spain). Flexible bags of a multilayer OPP25 μm + OPP25 μm packaging material with active compounds were prepared by GOGLIO, identical in size and materials used as those used for commercial purposes by LACASA. A special adhesive with the GTE incorporated was used to build the multilayer. The system is under patent petition. Commercial trays and the same multilayer flexible material as that used in the current application without any active agent were also used as blank for the long-term experiment (16 months). Two sets of packaging systems were used in the same format and size as the current packaging (36 plastic bags of 1 kg and 36 trays of 1 kg), half of them (18 bags and 18 trays) with the active components and the other half without the active components (Table 1). The plastic bags were made by thermosealing the multilayer once filled in with the food, while in the trays only the lid was made with the new antioxidant multilayer. This lid was thermosealed to the tray after filling. All the products were produced immediately before packaging. The packaging process was done at pilot plant scale. Room temperature (23 °C) was used for the study, as these chocolate products are usually kept in the linear of supermarket without refrigeration or additional care. This temperature was selected as the worst scenario. The current shelf life of these products is 9 months. The present study lasted for 16 months.

**Table 1**
Details for the experiments using active and non-active packaging materials.

| | | |
|---|---|---|
| Starting date for the experiment: | 24/02/2013 | |
| Best before: | 24/10/2014 | |
| Sample size: | 1 kg bags | 1 kg trays |
| Samples n°: | 36 | 36 |
| Samples types: | 18 bags with active material in the adhesive | 18 trays with active material in the adhesive |
| Non-active | 18 bags without active material in the adhesive | 18 bags without active material in the adhesive |

## 3. Experimental design

The evaluation of this new active material was based on a long-term monitoring of key components of the samples involved in the food quality due to lipid oxidation. The first step was to evaluate the radical scavenging properties of the new multilayer produced by GOGLIO. Once demonstrating the antioxidant performance, this material was used for packaging real food produced by LACASA. For the dark chocolate peanuts volatile compounds (i.e., hexanal, pyrazines and related compounds) and the fatty acid profile were used. For milk chocolate cereal samples only the volatile compound profile (i.e., hexanal, pyrazines and related compounds) was used. These two types of monitored chemicals are key components in the oxidation process of fatty food.

Volatile analysis profile was performed monthly for all the samples (e.g., four analysis for four samples, two of each type of product and each type of material "active/non-active"), whereas the analysis of fatty acid profile was performed every 3 months and only for the "dark chocolate peanut" samples (two samples, one with the active material and the other with the non-active material and three independent replicates in each case). The experiment started on 24th February 2013 and lasted for 16 months. The "best before" date was in all cases 24th September 2013. The study lasted until the end of May 2014.

### 3.1. Chemicals and reagents

Green tea extract (GTE) was supplied by Taiyo Green-power Co. Ltd. (Jiangsu, China). Multilayer active and non- active packaging bags and the multilayer film for the lid of the trays were produced by Goglio S.p.A (Daverio, Italy). Hexanal and the fatty acids methyl ester mixture (FAME) used as standard for quantification purposes were supplied by Sigma-Aldrich S.A. (Madrid, Spain). High purity quality solvents such as dichloromethane, cyclohexane, heptane and boron trifluoride were from Scharlau (Barcelona, Spain). Ultrapure water was obtained from a Milli-Q system (Millipore, Billerica, MA, USA).

### 3.2. Antioxidant evaluation

The antioxidant properties of the new polymer were measured by the free radicals method developed by Pezo, Salafranca, & Nerín, 2008. The method consists of generating an atmosphere enriched in free radicals from a $H_2O_2$ solution nebulized in a quartz tube. The generation of free radicals is enhanced by a photochemical reaction using UV lamps on the quartz tube. An inert gas carries the atmosphere through the plastic bag made from the polymer under evaluation and after this step the final gas bubbles into a solution of aqueous salicylic acid (SA).

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