LWT - Food Science and Technology 91 (2018) 34–39

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

FucoPol and chitosan bilayer films for walnut kernels and oil preservation

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ARTICLE INFO

Keywords:
Packaging
Bilayer FucoPol/chitosan
Oxygen barrier
Walnuts

ABSTRACT

Bilayer films composed of a bacterial exopolysaccharide (FucoPol) and chitosan were studied in terms of barrier material for walnuts (*Juglans regia L.*) preservation in opposition to a non-biodegradable commercial film used for that purpose (polyamide cast flexible-polyethylene - PA/PE 90). In experiments conducted under accelerated storage conditions (24 h of light, 33% RH, 38 °C for 14 days) using walnuts oil, the oxygen content in nitrogen flushed packages increased to 5–7% with both films. In addition, after one day, the oil stored in contact with 21% oxygen presented a peroxide value above the legal limit for olive oil in Portugal (15 meqO2 kg^{-1}), while the oil stored with bilayer and commercial films only present values above that limit at the end of the experiment. The oil content in conjugated dienes and trienes over time was also quite similar for bilayer and commercial films. Furthermore, sensory analysis performed on walnut kernels, stored in the same conditions as the oil, revealed non-significant differences in rancidity. The results have shown that the preservation capacity of the biodegradable bilayer FucoPol/chitosan films was equivalent to that of the non-biodegradable commercial ones, which makes them a promising sustainable alternative as packaging materials for walnuts.

1. Introduction

Walnuts possess a high economic interest in the food industry. Its global production is dominated by the USA and China and, according to the International Nut & Dried Fruit Council, global production of walnuts was 500,000 tonnes in 2012. Regarding EU, Germany accounted for 21% of walnut volume imports in 2014, being the leading importer in the EU and globally. Its consumer market for walnuts worth approximately €130 million in retail values, being the fifth largest global consumer after China, USA Turkey and France (CBI Market Information Database, Product Factsheet - Walnuts in Germany, 2014).

Walnuts are commercialized in-shell, shelled, in kernels form or grounded. In addition, they can be consumed as fresh fruit or toasted, as ingredient in bakery or even as flavour (Martínez, Labuckas, Lamarque, & Maestri, 2010; Mexis, Badeka, Riganakos, Karakostas, & Kontominas, 2009).

Walnut kernels are highly appreciated not only due to their good organoleptic characteristics, but also because of their health benefits, namely to reduce blood pressure and total cholesterol and to prevent cardiovascular diseases. These properties are associated with their chemical composition, in particular with oil and antioxidants (phytosterols and polyphenols). The oil content may vary from 52% to 74% according to the cultivar and origin (Bakkalbası, Yılmaz, Javidipour & Artık, 2012; Kang, Kim, You, Lacroix, & Han, 2013; Ling, Hou, Li, & Wang, 2014; Martínez et al., 2010).

The oil has a high polyunsaturated fatty acids (PUFAs) content, around 57.3–76.6 g/100 g. The overall and relative contents of PUFAs are important to economic and nutritional value of the nuts, once higher levels of PUFAs are more desirable due to their potential health benefits. In fact, walnuts are the only nuts that have significantly high content in omega 3 fatty acids, and they are the only nuts allowed to use a health claim in the European Union ("Walnuts contribute to the improvement of endothelium-dependent vasodilation" (artery health), based on daily consumption of 30 g of walnuts) (CBI Market Information Database, Product Factsheet - Walnuts in Germany, 2014).

However, high PUFAs content limits the nuts shelf life due to their susceptibility to oxidation. This fact leads to the most important quality parameter of walnuts conservation, lipid oxidation, which causes rancid taste and aroma that are unacceptable to the final consumer (Bakkalbası et al., 2012; Zwarts, Savage, & McNeil, 1999). The

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https://doi.org/10.1016/j.lwt.2018.01.020
Received 28 August 2017; Received in revised form 8 December 2017; Accepted 7 January 2018
Available online 09 January 2018
0023-6438/

oxidation reactions are dependent on external factors that are related essentially with oxygen concentration, temperature (Bakkalbası et al., 2012; Jensen, Sørensen, Brockhoff, & Bertelsen, 2003; Mexis et al., 2009), relative humidity (Maté, Saltveit, & Krochta, 1996) and light (Martínez, Barrionuevo, Nepote, Grosso, & Maestri, 2011).

Oxygen concentration is considered the most important external factor inducing lipid oxidation. As such, several strategies have been studied to decrease the oxygen effect, such as modified atmosphere packaging with low oxygen levels (composed mainly by nitrogen and carbon dioxide), vacuum packaging, or the use of oxygen absorbers (Jensen et al., 2003; Pastorelli et al., 2007). The availability of oxygen in the package can also be controlled by using oxygen barrier materials (Mexis et al., 2009) or a coating formulation (Kang et al., 2013). The rate of oxidation is independent on oxygen concentration at high oxygen partial pressure, but it is proportional to oxygen concentration at low oxygen partial pressure (Maté et al., 1996). Independently of the strategy used, it is essential to minimize oxygen contact with walnut kernels to extend their shelf-life.

As such, the use of an efficient oxygen barrier material in walnuts packaging is of major importance. Several barrier materials (with one or more polymers) have been studied, such as polyamide/polyethylene (PA/PE) (Bakkalbası et al., 2012; Ling et al., 2014), low density polyethylene (LDPE), polyethylene terephthalate/polyethylene (PET/PE) (Mexis et al., 2009), polyethylene (PE), ethylene-vinyl alcohol/low-density polyethylene(EVOH/LDPE) (Jensen et al., 2003), among others.

Beyond that, a wide variety of biopolymers has been studied to produce barrier materials, in particular, polysaccharides, due to their good barrier properties against oxygen at low or moderate relative humidity. In addition, these materials are biodegradable, making possible to contribute for reducing plastic waste in the end of service life (Ferreira, Alves, & Coelhoso, 2016). Bearing that in mind, it would be quite important to design and use biodegradable materials possessing simultaneously good barrier properties.

In this work, bilayer films composed by two biopolymers (FucoPol and chitosan) characterized in a previous work (Ferreira, Torres et al., 2016) were tested as alternative barrier materials. FucoPol is biodegradable anionic heteropolysaccharide with a high molecular weight, produced by the bacterium Enterobacter A47 (DSM 23139) using glycerol by-product from biodiesel industry as carbon source. It is composed by sugars (fucose, galactose, glucose and glucuronic acid) and acyl groups (acetate, succinate and pyruvate). (Torres et al., 2011).

The objective of this work was to evaluate the bilayer films of FucoPol and chitosan as barrier materials to be used in walnuts packaging, in parallel with commercial non-biodegradable PA/PE films currently used by producers. Storage experiments were carried out with walnut oil and kernels. The performance of the two barrier materials was evaluated in accelerated storage conditions (24 h of light, 33% RH and 38 °C), monitoring the oxygen content in the package, as well as, the oils peroxide value and oxidation compounds over time.

2. Materials and methods

2.1. Walnut kernels and oil

Fresh walnut (*Juglans regia L.*, cultivar Chandler) kernels were supplied by H. Reynolds de Souza, Estremoz, Portugal, and stored at 4 °C until being used. Oil from walnut kernels was extracted mechanically using a homemade pressing machine composed of screw and a nozzle of 5 mm. After extrusion, the pressing cake was discharged and the crude oil was centrifuged (15 min, 48384 × g). The clean oil was transferred into amber glass bottles, which headspace was flushed with nitrogen before closing. The bottles were stored at 4 °C before experiments for a maximum period of 24 h.

2.2. Bilayer films preparation

Bilayer films of FucoPol and chitosan were prepared by a two-step coating technique as described by Ferreira, Alves et al. (2016). Briefly, a Fucopol filmogenic solution composed of biopolymer (1.5% w/w) and citric acid (50% dry basis) was cast on a flat surface and dried at 30 °C until a firm but still adhesive surface was obtained. Afterwards, a chitosan solution containing the biopolymer (1.5% w/w), citric acid (50% dry basis) and glycerol (50% dry basis), was spread on top of the FucoPol layer and the bilayer was dried at 30 °C for 24 h.

2.3. Packaging preparation

Depending on the experiment, walnuts oil (15 mL) or walnut kernels (12 g) were transferred to home-made glass vessels (35 mm diameter, 6 cm height) without cover. The vessels possess an open vial-like (20 mm) where Mininert® Valve (Supelco, USA) was inserted. In order to have a sealed vessel, after introducing the walnuts kernel or walnuts oil, the top of the glass vessel was covered with the test film (bilayer film of FucoPol and chitosan or commercial film) and sealed with a commercial aluminum foil (Avery Dennison, USA). The effective mass transfer area was 2 cm^2. The leak tightness was tested to ensure that the oxygen transfer took place exclusively through the test films.

The permeability to oxygen of the commercial film (polyamide cast flexible-polyethylene - PA/PE 90) is lower than 4.6×10^{-17} mol m/(m^2 s Pa) (according to the supplier), and that of the bilayer film was reported by Ferreira, Alves et al. (2016) to be 4.7×10^{-17} mol m/(m^2 s Pa). The flasks with the samples (oil or walnut kernels) were flushed with nitrogen to start with nearly zero oxygen content in the beginning of the experiments.

2.4. Storage experiments

Two different experiments were carried out. One of them with extracted walnut oil and the other with shelled walnut kernels. In each case, samples totally exposed to air (labelled as No Package), sealed with bilayer films of FucoPol and chitosan (labelled as Bilayer) and sealed with commercial film (polyamide cast flexible-polyethylene (PA/PE 90), purchased from AlemPack (Portugal)) (labelled as Commercial) were used.

For fast lipid oxidation monitoring, unpacked and packed walnut oil was stored in a climate chamber (Cassel, Germany) set to 38 °C and 35% relative humidity (RH) for 14 days with 24 h of light. Oxygen content inside the package and oil analysis (peroxide value, primary and secondary oxidation products) were performed on the 1st, 7th and 14th days of storage. Three replicates of each day were analyzed. In the second experiment, shelled walnuts were packed in the same vessels, with the same sealing method. Unpacked walnuts kernels were maintained at the same light and temperature conditions. Sensory evaluation of packed and unpacked walnuts kernels was performed at the 7th and 11th days (to avoid complete oxidization). Four replicates of each day were analyzed.

2.5. Analytical methods

2.5.1. Oxygen content

The oxygen content inside the glass vessels was measured along time using a headspace gas analyser Checkmate 3 (Dansensor, Ringsted (Denmark)). Gas analysis was performed by pulling out a headspace gas sample by piercing a syringe needle through Mininert® Valve attached in the glass vessels.

2.5.2. Peroxide value of walnut oil

The peroxide value (PV) was determined according to the standard NP EN ISO 3960 (2010) “Animal and vegetable fats and oils - Determination of peroxide value – Iodometric (visual) endpoint