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Effect of antioxidant active films on the oxidation of soybean oil monitored by Fourier transform infrared spectroscopy

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ABSTRACT

An active film prepared from waterborne polyurethane incorporated with different concentrations of butylated hydroxytoluene (BHT) and α-tocopherol was developed, and the films' antioxidant characteristics were studied using soybean oil as food model. The release behavior of additives from such films was studied using isooctane as a simulant fatty food. Antioxidant activity of the films into soybean oil at three experimental conditions was monitored by FTIR spectroscopy. Induction time and the kinetics of the oxidation process were followed using different bands of the FT-IR spectra. Films incorporated with 2 wt.% of BHT or α-tocopherol showed enough antioxidant activity to preclude oil oxidation during 60 days at 60 °C in the dark. The results showed that this type of active films could be used for food preservation as part of a packaging containing oils or oily related products.

1. Introduction

The active packaging is one of the most novel concepts that has arisen in the food package industry, answering to the continuous demands of the consumers for more fresh products and of the producers with extended shelf life (Vermeiren et al. 1999; Brody et al., 2001; Ahvenainen, 2003).

Beneficial interactions between food and package are based on the regulation of the headspace content (O_2, CO_2, ethylene), the control of humidity, the action of diverse enzymes, liberation of antimicrobial or antioxidant substances, among others. This approach can reduce the addition of large amounts of food additives that are usually incorporated into food.

Originally, inside the package only physicochemical changes occurred due to the natural evolution of the product, with this new technology the headspace environment will be improved owing to the package (Rooney, 2005).

Oxidation of lipid compounds in the packaged foods could be controlled by the use of antioxidant additives. If antioxidants are included in the matrix of the packing material and a controlled slow liberation is achieved, the contained product will see its shelf life increased, without adding unnecessary quantities of the antioxidant. Synthetic antioxidants such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) although very effective, are not without side-effects (Shlian and Goldstone, 1986) and therefore it should be limited by regulating the dosage (controlled release for example) or by substituting them with natural antioxidants like tocopherols.

Oils and fat oxidation is one of the most noticeable degradation processes in food industry, due to the generation of undesirable flavors and changes in nutritional aspects, with consequences on health, nutritional quality and consumer's choice (Gómez-Alonso et al., 2004). During lipid degradation, different processes occur simultaneously: oxidation of some compounds, hydrolysis of triglycerides and *cis/trans* isomerization of unsaturated fatty acids (Li et al., 2013; Velasco and Dobarganes, 2002).

The lipid degradation process occurs at low rate at room temperature, and hence accelerated methods should be employed to estimate the oxidative stability of the product or the induction time of the autoxidation reaction in a relatively short period of time (Frankel, 1993). Several physical or chemical parameters, such as temperature can be used to increase the rate of the reaction and, consequently, the development of rancidity. In the literature,

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several approaches to predict oil oxidative stability can be found depending on the interest in storage stability or processing performance. Oils are treated at 100 °C or lower to evaluate storage stability; in contrast, higher temperatures are used to evaluate oil performance in food processing such as frying (Climaco-Pinto et al., 2010; Guillén and Cabo, 1999; Innawong et al., 2004; Moros et al., 2009; Moya-Moreno et al., 1999; Vlachos et al., 2006).

Infrared spectroscopy has been proven to be an important tool in the assessment of the quality and composition of various edible oils, as well as in the monitoring processes in the food industry due to low cost, excellent performance and ease of use compared with other methods (Maggio et al., 2009; Van de Voort, 1992). Bands in the infrared spectrum have been reported for edible oils in different studies (Guillén and Cabo, 1999, 2002; Innawong et al., 2004; Lerma-García et al., 2010). The studies also describe how they are modified through the process of oxidation. Following these changes in the spectra, a qualitative and quantitative determination of the progress of oxidation is possible.

BHT-impregnated film has shown that retards lipid oxidation of a packaged oatmeal cereal through its migration from the product via an evaporation/sorption mechanism (Lee et al., 2004). BHT is a small molecule that exhibits high mobility and therefore has a tendency to migrate rapidly from packaging materials into foods (Wessling et al., 1998). Slow release of BHT from the package will help extend the shelf-life of the food product. The use of antioxidant packaging has also been proposed to reduce lipid oxidation in milk (Granda-Restrepo et al., 2009).

Polyurethanes (PUs) are versatile polymers prepared from condensation of polyisocyanates and polyols. The properties of these raw materials and their ratio, expressed as NCO/OH, determine the final properties. PU based materials were not used for contact in foods probably due to migration of different components and additives used during their manufacturing. However, several polymeric materials were tested by Gramiccioni et al. (1986) using olive oil and isooctane as a liquid simulant for fatty foods and they found that the global migration values obtained with olive oil and isooctane for polyurethane were much lower than those for the PVC based materials. This situation is currently changing as a consequence of gained knowledge on PU synthesis and the availability of new raw materials. General properties of polyurethanes can be modified without using plasticizers or additives just selecting the raw materials, reducing in this way the global migration and allowing them to be used in contact with food. The urethane moiety is a suitable functional group to promote interactions with other molecules and in particular with active principles capable of forming hydrogen bonds, modifying in this way their releasing behavior. On the other hand, polyolefin polymers like polyethylene, used frequently in food industry, do not have this possibility.

Bearing in mind all these facts, in this work, polyurethane films were added with different concentrations of BHT or α-tocopherol and immersed in soybean oil. The progress of the oxidation under different conditions was evaluated by FT-IR/ATR spectroscopy. The kinetics of the antioxidant release from the polyurethane films was also studied using isooctane as liquid simulant for fatty foods.

2. Materials and methods

2.1. Active films preparation

Polymer films were prepared from a waterborne polyurethane dispersion synthesized in our laboratory as described in previous papers (Pardini and Amalvy, 2008; Peruzzo et al., 2010). The mechanical and thermal properties of the polyurethane matrix were also discussed in the above mentioned works. Incorporation of the active agent to the polymeric matrix was made by dissolving the antioxidant compound in the minimum amount of acetone and by adding this solution, drop by drop, to the polymer dispersion under magnetic stirring at room temperature for about 10 min. The dispersion was then placed on a Teflon® plate for casting. Evaporation of water and acetone was made at room temperature and in the darkness; this process took about 24 h. The formed film was cured at 60° C for 48 h to ensure the complete coalescence of the polymer.

Samples containing 1, 2 and 5 wt.% on final film of antioxidant compound were prepared.

2.2. Oxidation studies

Twenty-five mL of commercial soybean oil were placed in glass bottles of 50 mL with an open surface area of 12 cm^2 in a dry place. The oil samples were exposed to air and active films of 3.5 cm diameter and 200 μm thickness containing 1, 2 or 5 wt.% of the active component (BHT or α-tocopherol) were immersed in the oil samples. A control sample (PU film without antioxidant) was also included and experiments were run by triplicate.

It has been shown that oxidation of vegetable oils is promoted by light, temperature and oxygen availability (Pignitter et al., 2014). In order to evaluate how these factors affect the oxidation degree, samples were kept opened under three different environmental conditions at RH 60–70%:

1. Dark place at 25 °C.
2. In a transparent glass bottle (25 °C) exposed to ambient room light at day time for 10–12 h/day.
3. Dark place at 60 °C.

2.3. FT-IR spectra acquisition and data analysis

Periodically, with previous agitation of the bottle, the infrared spectrum of the soybean oil was collected. Spectra were acquired against air reference using a Spectrum One spectrophotometer (Perkin Elmer, USA) equipped with a KBr beam-splitter and DTGS detector. A 100 μL oil drop was deposited on the diamond single reflection ATR accessory. The wavenumber range measured was 4000–650 cm^{-1} with 4 cm^{-1} resolution and 32 scans accumulated. EZ OMNIC 7.4.127 software (Thermo Electron Corporation) was used for data treatment. The ATR crystal and its surroundings were thoroughly cleaned between samples.

Vibrational spectra of oils were compared to the control zero time oil. The appearance or modification of certain bands allows determining the development of oxidative process.

2.4. Determination of the induction time by the Quality Control tool

With the purpose of avoiding experimental errors in the determination of the moment where the spectra begin to change as compared to the "zero time" sample, Quality Control tool of the EZ Omnic7.4.127 software was used. This tool allows a rapid determination of induction times without processing spectra. The fingerprint region (1500–650 cm^{-1}) of the IR spectra was used to compare the fresh oil with the other samples. The critical value of correspondence was 95%.

2.5. Determination of kinetic parameters from infrared data

Kinetic parameters and induction times were calculated using the values of absorbance of different bands associated to species formed during the oxidation processes. At moderate temperatures, the lipid autoxidation follows a pseudo-first-order kinetic, independent of the oxygen pressure (Velasco and Dobarganes, 2002; Frankel, 1998; Román-Falcó et al., 2012). If other oxidation