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Monitoring lipid oxidation in a processed meat product packaged with nanocomposite poly(lactic acid) film

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ABSTRACT

One of the most detrimental processes in fatty foodstuffs is lipid oxidation, which occurs during production and storage, and influences food composition and safety. Polylactic acid (PLA), a commercially available biopolymer, is biodegradable thermoplastic aliphatic polyester derived from renewable resources. Polymer layered silicate (PLS) nanocomposites have shown potential for enhancing physical, chemical, and mechanical properties of both conventional materials and biopolymers. In the present work nanocomposite films were prepared by incorporating unmodified montmorillonite clay (Cloisite® Na^+) in the PLA. Moreover, the lipid oxidation status of a processed meat product packaged with a film incorporating this nanocomposite was evaluated. In line with this, hexanal, Thiobarbituric Acid Reactive Substances (TBARS) and *p*-anisidine value were monitored after packaging salami during different storage times (15, 30, 60 and 90 days). The results of this study showed that the presence of montmorillonite (MMT) in the polymer film can reduce the lipid oxidation of processed meat products, extending their shelf life and, thus, suggesting that the new film is a potential good alternative to conventional bioplastics.

1. Introduction

In recent years, the concern to provide consumers with high quality foodstuffs has led to the adoption of measures to limit the oxidation phenomenon during the processing and storage of products [1]. The use of biodegradable materials for food packaging is considered an environmentally correct alternative, since it reduces the use of polyolefinic plastics as packaging materials [2]. PLA, a commercially available biopolymer, is a biodegradable thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States and Canada), tapioca roots, chips or starch (mostly in Asia), or sugarcane (in the rest of the world) [3]. Natural fibre reinforced PLA based biocomposites are widely investigated by the polymer scientists in the last decade to compete with non-renewable petroleum based products [4].

During the last decades, the interest in polymer layered silicate (PLS) nanocomposites had an exponential growth since they have been shown to enhance physical, chemical, and mechanical properties of both conventional materials and biopolymers. Polymer nanocomposites are reinforced by nanometric fillers, one of the most used is montmorillonite (MMT) not only because it is an environmentally friendly material, occurring naturally, but also because is readily available in large quantities. It has been already used in the literature to overcome some weaknesses of PLA films such as poor barrier properties [5]. In this paper unmodified montmorillonite clay Cloisite® Na^+, was incorporated in PLA film and the obtained nanocomposite films were used to investigate their effect as packaging materials in the preservation of a model fatty food. In fact, one of the most detrimental processes in fatty foodstuffs is lipid oxidation. The lipid oxidation results from a spontaneous and inevitable event that the fatty foods undergo during the processing and storage and which has as main consequence the modification of the original flavour and the appearance of rancid odours and tastes. These changes represent for the consumers and for the food industry an important cause of depreciation or rejection. This phenomenon has a direct implication on the commercial value of the fatty substances and the products that are formulated from them (e.g. foods, cosmetics, medicines) [6]. Consequently, lipid oxidation has long been recognized as a leading cause of quality deterioration of the food

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and is often the decisive factor in determining food shelf life [6]. Lipid oxidation is a complex process whereby unsaturated fatty acids react with molecular oxygen via a free radical mechanism [7]. As result of lipid oxidation, a complex mixture of lipid oxidation products is produced.

It is well known that barrier properties of the packaging material play a major role in determining the shelf life of a food product. In particular, in order to control lipid oxidation, it is important to improve the barrier properties of packaging films, such as permeability of moisture and gases across the packaging material [8]. One of the most important control parameters for oils, fats and oilseeds is moisture because the stability of these foods decreases with increasing moisture content [9]. To this aim, in this paper low amount of layered nanoclays has been incorporated in polylactic acid in order to improve the water barrier of the packaging film. In fact, Sonjui and Jiratumnukul [10] reported a reduction by more than 14% in the water vapor transmission rate of PLA bionanocomposite coating films reinforced with 0.1% (w/w) of Cloisite 30B. Qiuhui et al. [11] showed that a novel nanocomposite-based packaging prepared by blending polyethylene (PE) with montmorillonite significantly decreased the oxygen and water vapor permeability. In this paper the effect of PLA/MMT films in the packaging of sliced salami has been investigated. In particular, salami slices were packaged with PLA/MMT films and with a control film (PLA). After different storage times (0, 15, 30, 60 and 90 days), salami slices were analyzed regarding their hexanal, TBARS and *p*-anisidine value and the obtained results were correlated with water barrier properties data of the nanocomposite films.

2. Material and methods

2.1. Preparation of the PLA/cloisite® Na^+ film

The pristine clay (Na^+-montmorillonite), hereafter named MMT, was purchased from Southern Clay Products, Inc., TX and used without further modification. NatureWorks™ Poly (L-lactide) polymer 2002D was supplied by Cargill Dow LLC (Minnetonka, MN). The density of the PLA was 1.25 g cm^{-3}. As an alpha hydroxyl ester, PLA tends to hydrolyze at elevated temperatures and high relative humidity. For this reason, PLA pellets were dried at 50 °C at least for 12 h in vacuum prior to use.

PLA/MMT (Cloisite® Na^+) composite films were prepared by direct melt processing. MMT (powder form) and PLA (pellet form) were first mixed at 180 °C and at 60 rpm for 5 min in an internal mixer (Rheomix® 600 Haake, Germany) with a volumetric capacity of 50 cm^3. After homogenization of PLA and MMT particles, the films with thickness of 100–150 μm were prepared by compression moulding using a Collin P300P press at 180 °C and at 5 MPa for 3 min, cooled down for 10 min at 10 °C min^{-1} and 1 MPa. Films of pure PLA (as control) and films containing 5 wt% of MMT were prepared and tested afterwards.

2.2. Packaging of salami

To test the effectiveness of the nanocomposite films, the selected model food was the salami due to its high fat content. Salami was purchased, already sliced, in a commercial area of Lisbon (Portugal). The selected salami presented the following nutritional composition per 100 g: protein 23.5 g, total lipids 26.5 g, carbohydrates 4.9 g and 3.9 g salt.

Salami slices (approximately 10 g each) with a thickness of approximately 2 mm each, were placed in direct contact with nanocomposites films containing 5% MMT (w/w) and a control film (PLA without nanoclay). Subsequently, they were packed in a vacuum to allow good contact between the films. All prepared samples were stored at 5 °C, protected from light. The samples were analyzed after 0, 15, 30, 60, 90 days of storage for evaluation of oxidation status of salami packaged with either the control films or films with nanoclays.

2.3. Effectiveness of the PLA-based films against lipid oxidation

The effectiveness of the PLA and PLA-MMT films against lipid oxidation was carried out by three different methods: *p*-anisidine value, TBARS assay and hexanal monitoring.

2.4. p-anidisine value

p-anisidine value, a spectrophotometric analysis method measuring the absorbance at 350 nm, was used following the official method (AOCS Official Method Cd 18–90), [12]. The *p*-anisidine in acetic medium forms a yellow complex with the aldehydes having two conjugated double bonds, in particular with *trans*, *trans*-2,4-decadienal resulting from the degradation of linoleic acid.

In order to determine *p*-anisidine value, the fat was extracted from the salami slices packaged with either the control films or films with nanoclays. Ten grams of sample was shaken for 1 h with 100 ml of petroleum ether. The solution was filtered into an evaporator flask with Whatman No. 4 filter to which anhydrous sodium sulfate was added to retain the sample water. The petroleum ether was evaporated at 40 °C. The fat was kept at 5 °C, protected from light, until the tests to obtain *p*-anisidine value were performed.

The determination of the *p*-anisidine value was performed according to British Standard method BS 684-2.24-1998 (British Standard Method 1998) [13]. First the *p*-anisidine solution is prepared by weighing 50 mg of *p*-anisidine into a 20 ml flask and make up the volume with acetic acid. To 0.5 g of fat (previously extracted), 25 ml of *n*-hexane was added and the solution was placed 5–10 min in the ultrasonic bath at room temperature until the fat dissolves. The absorbance of the solution is measured at 350 nm against n-hexane. One ml of the solution of *p*-anisidine in acetic acid was added to 5 ml of the sample solution and it was stored in the dark for 10 min at room temperature. For the control test, 1 ml of the solution of *p*-anisidine was added to 5 ml of n-hexane. Finally, the absorbance of the samples against the control test was measured. All analyzes were performed in triplicate.

The *p*-anisidine value was calculated according to the following equation:

$$AV = 25(1.2Abs_2 - Abs_1)/m \quad (1)$$

where:
AV - value of *p*-anisidine;
Abs_2 - absorbance of the sample after 10 min of reaction;
Abs_1 - initial sample absorbance;
m - amount of fat used in the test (in g).

2.5. Thiobarbituric acid reactive substances (TBARS) assay

TBARS assay was based on the spectrophotometric measurement of a complex formed by the reaction between Thiobarbituric acid (TBA) and malondialdehyde (MDA) according to the method of Miller [14]. Malondialdehyde (MDA) is formed as a result of the degradation of polyunsaturated fatty acids, therefore this test is a measure of the oxidative status of a sample.

About 5 g of packaged salami was homogenized with 50 mL of trichloroacetic acid (10%) in 0.02 M of orthophosphoric acid using an Ultra-Turrax (IKA DI 25 basic, Werke GmbH & Co, Germany). Then, the solution was filtered through filter paper (Whatman n° 1) and then 5 mL of this solution was homogenized with 5 mL of TBA aqueous solution 0.02 M and heated at 100 °C for 40 min. Afterwards, solutions were cooled down for 10 min and the concentration of the substances that have reacted with TBA after heat treatment was calculated by measuring the absorbance at 530 nm. A standard curve of 1,1,3,3-tetraethoxypropane (TEP) was prepared with rate concentration ranging from 0 to 5 μg/mL. Results were expressed as mg malondialdehyde (MDA) per kg of salami (mg MDA/kg).