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Biodegradation behavior of three-layer sheets based on gelatin and poly (lactic acid) buried under indoor soil conditions

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ABSTRACT

The biodegradation of three-layer sheets composed by glycerol-plasticized bovine gelatin film as the inner layer and coated with two outer layers of poly(lactic acid) (PLA) was examined under indoor soil burial conditions during 120 days, using the natural soil microflora as degrading medium. The residual degraded samples of the multilayer and individual components were taken regularly from the soil to determine water uptake, weight loss, variations in thermal properties and morphology. The multilayer sheet exhibited reduced water uptake as compared to the gelatin counterpart, which was associated with the protection of the middle gelatin layer against water by the hydrophobic PLA layer at both sides. The gelatin layer almost disappeared after 25 days, while the pure PLA layer suffered marginal weight loss on day 120 in soil. On the contrary, the multilayer sheet was degraded to a much greater extent, leading to an overall mass reduction of approximately 20% at the end of the experiment. The presence of gelatin in the multilayer seems to enhance water availability around the three-layer sheet soil micro-environment, inducing gelatin hydrolysis (chemical and enzymatic) which favors the abiotic hydrolysis of PLA, and, in turn, possibly stimulates the action of more active soil microorganisms against PLA. This was experimentally confirmed by the presence of filamentous (actinomycete and fungi) microbes on the surface of the multilayer. The glass transition temperature of the degraded multilayer samples slightly increased while the degree of crystallinity augmented significantly up to 78% on day 120, evidencing the crystallization of the amorphous PLA induced by bio/degradation in soil.

1. Introduction

Multilayer films have gained relevance in many industrial applications, especially in the fresh food packaging industry, for extending shelf-life [1]. Lamination is widely used to improve polymeric films performance by combining the properties of several types of layers into one film or sheet [2–5]. However, while the combination of various layers is required for good food preservation, the recyclability or biodegradability of the multilayer packaging could become compromised. The impact of packaging waste on the environment can be minimized by prudently selecting materials and reviewing packaging expectations in terms of environmental impact [6–8].

Polymers derived from natural products, such as carbohydrates and proteins, offer the greatest opportunities as components of multilayer structures since their biodegradability and environmental compatibility are assured. Protein films are excellent oxygen and aroma barriers at low relative humidity with potential to replace synthetic oxygen-barrier components in multilayer formulations. Nevertheless, such property fails in high moisture environments due to the hydrophilic character of most proteins [4,9]. In an attempt to overcome this issue, numerous studies have focused on the use of bio-polyesters as protective layers of protein films, including three-layer films from a soybean protein isolate (SPI) laminated with poly(lactic acid) (PLA) by means of a solvent-casting procedure [3,10]; bi-layer PLA-SPI films obtained by casting [7], polyhydroxyalkanoates (PHAs)- ultrathin zein fibers [5] and bi-layer Bioflex™-isolate whey protein films (IWP) [8]. Most of these materials have proven to be biodegraded under the stimulus of an environmental trigger after use [7,8].

In a previous work [4], the authors described the design and performance of a biodegradable, high barrier, self-adhesive, three-layer sheet based on glycerol plasticized bovine gelatin layer acting as the oxygen barrier component and PLA as the outer layers

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produced by compression molding, as a potential thermoforming packaging solution. The favorable combination into a multilayer material enhanced the oxygen barrier of the pure PLA component (a limiting factor for PLA packaging applications), improved moisture resistance, and enhanced the mechanical and impact properties of its plasticized gelatin counterpart [4]. To consider such a multilayer sheet as a viable packaging material, it must retain the physical properties during the in-use period and ensure that lamination does not compromise the inherent biodegradability of the individual components under specific conditions, such as in indoor soil burial experiments.

The susceptibility of gelatin to the action of enzymes (proteases) present in a variety of micro-organisms has been well documented [11]. Several studies have centered on the effect of chemical modifications on the rate and extension of gelatin films biodegradation [12,13]. Conversely, the role that soil microorganisms play in PLA degradation is unclear and remains controversial [14]. PLA degradation is generally believed to follow a two-step mechanism involving first an abiotic process, which comprises the chemical hydrolysis of PLA, followed by the biotic assimilation of polymer break-down products by the micro-organisms, generating carbon dioxide, water and biomass under aerobic conditions [14,15]. As asserted by Tokiwa and Calabia [16], PLA-degrading microorganisms are not widely distributed in the natural environment and so, PLA is less susceptible to microbial attack in the natural biotic medium than other microbial and aliphatic polyesters. Other studies have suggested that some microbial enzymes are capable of directly degrading high molecular weight PLA [17,18]. Reports on the biodegradability of PLA in soil where temperature does not exceed 30 °C remain scarce. Ho and Pometto [19] found that about 20% of the PLA film was mineralized to CO_2 after 182 days in soil in a laboratory respirometer at 28 °C. In South Finland, the degradation of PLA in soil under real conditions was followed by the evaluation of the appearance of lactic acid and lactoyl lactic acid with time [20]. After 20 months, lactic acid and lactoyl lactic acid appeared as a result of hydrolysis, but the amount of lactoyl lactic acid decreased with time due to the biotic attack [20]. The long-term degradation of PLA films and fibers in natural Mediterranean soil (where air and soil temperature never exceeded 40 °C and 21 °C, respectively) and in simulated soil burial experiments was followed for 11 months by Rudnik & Briassoulis [21]. The slow degradation rate of PLA films exposed to real field conditions and simulated soil burial, suggested that materials need much more time and/or higher temperatures to achieve higher degradation levels, most likely because the degrading temperature is below PLA glass transition temperature (*Tg*) [21]. Karamanlioglu and Robson [14] examined the degradation of PLA coupons in a range of temperature (25–55 °C) in soil and compost. Findings support the direct role of temperature in PLA biodegradation, being more relevant at temperatures above PLA *Tg*. This study suggests that microbes can directly enhance degradation of high molecular weight PLA over and above chemical hydrolysis at elevated temperatures and that microorganisms in compost are more active in this process as compared to soil.

Based on the considerations outlined above and the potential industrial applications of the three – layer sheets based on PLA outer layers and plasticized gelatin inner layer, the main objective of the present study was to analyze the biodegradation of the multilayer sheet under indoor soil burial experiments. Biodegradation patterns in characterized soil were evaluated through weight loss determination and water sensitivity was assessed by measuring the water uptake at selected exposure times. Thermal properties, crystallinity, visual aspect, as well as morphology changes were followed on residual materials.

2. Experimental

2.1. Materials

Bovine hide gelatin (Ge) type B was kindly supplied by Rousselot (Argentina), Bloom 150, isoionic point (Ip) 5.3. Poly (lactic acid) (CML PLA) was purchased from Hycail Finland Oy (Turku, Finland) and used as received. Glycerol analytical grade (Gly, 98%) was supplied by DEM Chemicals (Mar del Plata, Argentina).

2.1.1. Sheets formation

Laminate sheets were prepared through a two-step process described in the previous work by the authors [4]. In the first step, the individual layers were separately obtained by thermo-compression. Additionally, the outer PLA layers and the glycerol (Gly) plasticized gelatin inner layer, Ge-30Gly, were stacked together and, subsequently, heat-compressed to the desired thickness. Before processing, PLA pellets were oven dried under vacuum at 60 °C for 4 h. Then, 4–5 g samples of PLA were placed between two stainless steel plates coated with a Teflon film and molded into sheets (30 cm^2) at 180 °C in a hot press (EMS, Buenos Aires, Argentina) using an aluminum frame to regulate the target thickness (0.150 mm). The material was kept between plates at atmospheric pressure for 2 min until melting and then it was submitted to the following pressure cycle: 3 MPa for 1 min, 5 MPa for 1 min and 10 MPa for 3 min. Finally samples were quenched under pressure (10 MPa) up to room temperature (25 ± 2 °C) and stored in a desiccator. Regarding the plasticized-gelatin layer, it was obtained under conditions similar to those previously described [13]. Gelatin powder and glycerol (30 wt. % on gelatin dry basis) were mixed together by using a kitchen mixer (M.B.Z., San Justo, Buenos Aires, Argentina) at low speed (150 rpm) for 24 h and at ambient temperature (25 ± 2 °C). The Ge-30Gly blends were thermo-molded into sheets (30 cm^2) at 120 °C in the same hot press above mentioned and under the following press cycle: 5 min at atmospheric pressure and 10 min at 5 MPa. Subsequently, samples were quenched up to room temperature (25 ± 2 °C) at atmospheric pressure and kept in a desiccator.

In the second stage, PLA and Ge-30Gly individual layers were piled together and thermo-compressed with no need to add any adhesive between layers [4]. An aluminum frame was used to control de final thickness of the multilayer (0.45 mm). Processing temperature was set at 100 °C, slightly above both gelatin and PLA glass transition temperatures [4,22]. Compression was achieved by applying 10 MPa for 10 min, followed by a cooling step up to room temperature at atmospheric pressure. PLA/Ge-30Gly/PLA sheets (thickness = 0.465 ± 0.046 mm), were stored in an environmental chamber under controlled temperature (25 ± 2 °C) and relative humidity (65 ± 2% RH) before testing.

Control PLA and Ge-30Gly sheets were obtained under similar conditions than those described for the individual components of the multilayer. For comparison reasons, thickness values were fixed at the same level of that of the multilayer, being 0.0416 ± 0.028 mm and 0.428 ± 0.018 mm for PLA and Ge respectively. Control samples were kept under similar storage conditions than multilayer sheet (25 ± 2 °C and 65 ± 2% RH) before testing.

2.2. Indoor soil burial

Biodegradation was studied by means of indoor soil burial experiments [6,13,23]. This strategy is a good approach to test biodegradability under real soil environment when biodegradation cannot be measured and quantified in the way proposed by the standard respirometric testing methods. The aerobic degradation of individual layers and multilayer sheets was carried out in a