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Effect of the state of water and relative humidity on ageing of PLA films

J.R. Rocca-Smith [a,b], N. Chau [a], D. Champion [a], C.-H. Brachais [c], E. Marcuzzo [b], A. Sensidoni [b], F. Piasente [d], T. Karbowiak [a], F. Debeaufort [a,e,*]

[a] Univ. Bourgogne Franche-Comté, Agrosup Dijon, UMR PAM A 02.102, Esplanade Erasme, 21000 Dijon, France
[b] Department of Food Science, University of Udine, Via Sondrio 2/A, 33100 Udine, Italy
[c] Univ. Bourgogne Franche-Comté, ICMUB UMR-CNRS 5260 EMMD, 9 Allée Alain Savary, 21000 Dijon, France
[d] Taghleef Industries, Via E. Fermi 46, 33058 San Giorgio di Nogaro (UD), Italy
[e] Univ. Bourgogne Franche-Comté, IUT Dijon-Auxerre, dpt BioEngineering, 7 Blvd Dr Petitjean, 21078 Dijon Cedex, France

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ABSTRACT

Various types of food are now commercialized in packaging materials based on poly(lactic acid) (PLA) due to its eco-friendly nature. However, one of the main limitations related to PLA is its reactivity with water. For food applications, it is of critical importance to better understand the hydrolysis of PLA driven by water molecules either in liquid or in vapour state. This work focuses on the modifications of PLA induced by water when simulating contact with semi-dry foods ($a_w \approx 0.5$), high moisture foods ($a_w \approx 1$) and liquid foods ($a_w \approx 1$). This study undoubtedly shows that both the chemical potential of water and its physical state influence the hydrolytic degradation of PLA films. From a practical point of view, PLA packaging is very well suited for semi-dry foods, but is highly sensitive to high moisture and liquid foods.

1. Introduction

Food industry is always interested in using the most suitable and performing packaging for preserving the quality of the food products over their shelf life. The increase in the environmental concern over the past decades is pushing towards the development of new packaging systems with eco-friendly characteristics, such as renewability, biodegradability and compostability (Cozar et al., 2014). The main challenge is to develop a packaging material, having a good balance between its durability and biodegradability, to guarantee the quality of various food products and to ensure an easy treatment of wastes with low environmental impact (Kale et al., 2007). This means that a new challenge is to find good adequacy between the food shelf life and the packaging shelf life.

A biopolymer with the potential to satisfy most of the overall requirements is poly(lactic acid), or PLA. PLA is a renewable and biodegradable polyester, which derives from carbohydrates sources such as starch corn, sugar cane and biomass waste like wood ships, bagasse and wheat straw (Castro-Aguirre, Iñiguez-Franco, Samsudin, Fang, & Auras, 2016). Thanks to enzymatic and microbial fermentations, these renewable resources are converted to lactic acid, the building block of PLA. The monomer is polymerized for obtaining PLA at high molecular weight (>100 kDa) via different chemical processes, such ring opening polymerization of lactides (*i.e.* cyclic dimers of lactic acid), direct condensation polymerization or azeotropic dehydration condensation (Auras, Harte, & Selke, 2004). Compared to other biopolymers, PLA shows interesting functional properties, reduced cost and easier facility to be industrially processed. It is considered as the most promising candidate for replacing conventional plastics and it is currently used as food packaging and food serviceware (Auras et al., 2004; Jamshidian, Tehrany, Imran, Jacquot, & Desobry, 2010).

Academia and industry are largely studying this polymer since a decade for tailoring its overall properties and increasing its applications (Rasal, Janorkar, & Hirt, 2010; Wang, Cui, & Bei, 2005). Although more efforts are still needed, the reached advances brought to PLA to play an important role in the current bioplastic market. The European Bioplastics Association (2016) recently reported that the world production of this polymer exceeded 207 thousand tons in 2014, representing the 12% of the bioplastic market. The main application of PLA is food packaging and it will probably remain the main use of PLA in the near future. PLA is also used in other areas such as medical, agriculture, textiles, 3D printing, electronics and automobile applications, which are all expected

* Corresponding author at: Univ. Bourgogne Franche-Comté, Agrosup Dijon, UMR PAM A 02.102, Esplanade Erasme, 21000 Dijon, France.
E-mail address: frederic.debeaufort@u-bourgogne.fr (F. Debeaufort).

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to have a higher importance in the following years (European Bioplastics Association, 2016).

Food corporations such as Danone (Germany), Del Monte (USA) and Noble Juice (USA), as well as leading food retailers such as Wal-Mart (USA), SPAR (Austria) and Auchan (France) are currently using PLA based packaging in some of their products (Castro-Aguirre et al., 2016). Various types of food products are currently packed and commercialized with PLA based materials. They are characterized by different physical states, a wide range of water activity (a_w), pH and composition. Some examples are potato chips (amorphous solids, a_w = 0.1–0.3), fresh salads and vegetables (biological gels, a_w > 0.99), yogurts (gels, a_w > 0.99), citrus juices (acid liquids, a_w = 0.97–0.99) and water (liquid, a_w > 0.99).

Although a general interest is noticeable to increase the trade food products packed in PLA, there is not enough information related to the interactions between food products and PLA based packaging available in the scientific literature. Such information is of relevant importance considering that one of the main limitations, related to the PLA packaged food, is the inherent water sensitivity of PLA that can compromise its stability. Even if PLA absorbs very small quantities of water (<1.5 wt%) (Auras et al., 2004; Witzke, 1997), PLA can interact with water molecules from the packed food, and can be hydrolysed during the time of storage. As a result of these chemical reactions, its performance for food packaging may be reduced during packed food storage, compromising therefore the quality and the safety of food.

The hydrolysis mechanism of PLA has been principally studied for applications of biomedical devices, such as implants and carriers of drug for controlled release (Göpferich, 1996; Li, 1999; Tsuji, 2010). Due to the importance in understanding the interactions between the polymer and the biological fluids, most of the available literature is focused on the hydrolysis of different types of PLA (*e.g.* amorphous, semi-crystalline, copolymerized) (Ramchandani, Pankaskie, & Robinson, 1997; Tsuji, Ikarashi, & Fukuda, 2004) having different shapes (*e.g.* microspheres, plates, cylinders) (Gonzalez, Ruseckaite, & Cuadrado, 1999; Grizzi, Garreau, Li, & Vert, 1995; Kucharczyk, Hnatkova, ZdenekDvorak, & Sedlarik, 2013) in aqueous or liquid buffer solutions, which simulate biological fluids (*e.g.* Ringer's solution, phosphate buffer solutions) (Migliaresi, Fambri, & Cohn, 1994; Tsuji & Ikada, 2000; Tsuji, Mizuno, & Ikada, 2000). Nevertheless, only few studies have been focused on the PLA hydrolysis carried out by water in the vapour phase (Copinet, Bertrand, Govindin, Coma, & Couturier, 2004; Ho, Pometto, & Hinz, 1999; Holm, Ndoni, & Risbo, 2006) and they generally do not consider PLA produced at large scale. This lack of information is of significant importance, since the interactions between packaging and water molecules of non-liquid foods are in the vapour phase.

Based on these considerations, the objective of this study was to better understand the modifications induced by water on the properties of PLA films during storage time, focusing on semi-dry foods ($a_w \approx 0.5$), high moisture foods ($a_w \approx 1$) and liquid foods in contact ($a_w \approx 1$) with PLA. In order to simulate these conditions, accelerated ageing tests were carried out for these three different wet environments. PLA films produced at industrial scale were placed at 50 °C in environments at 50 or 100% relative humidity (RH) or immersed in liquid water. The storage temperature chosen was able to accelerate the chemical reaction rates, without inducing significant modifications in the physical state of PLA. Indeed, transitions from the glassy to the rubbery states occurred at 5–10 °C higher than 50 °C. The first two conditions provided information related to the interactions between PLA and water in the vapour state, while the third one gave information regarding interactions with liquid water. The functional properties, the molecular weight distribution, the surface properties and the thermal events of PLA films were assessed over a 2 months storage period.

2. Materials and methods

2.1. PLA films

Semi-crystalline PLA films (D-level ≥4.25%) available in the market for food packing applications were used in this study. They were produced and supplied by Taghleef Industries (thickness = 17 μm, commercial name: Nativia NTSS, Udine, Italy). During production, films were subjected to a biaxial orientation and annealing to induce crystallization and to improve their mechanical properties. The number-average molecular weight ($\overline{M_n}$), the weight-average molecular weight ($\overline{M_w}$) and the polydispersity index (*PDI*) of initial PLA films was approximately 70,000 g·mol^{-1}, 160,000 g·mol^{-1} and 2.3, respectively.

2.2. Storage conditions of accelerated ageing test

Rectangular PLA films (21 × 15 cm) were stored up to 69 days (≈2 months) in different humidity conditions at 50 °C using microclimate chambers. The PLA samples were immersed in water or placed in environments at ≈50 or 100% relative humidity (RH) environments. These different storage conditions were maintained using NaBr (50.9% RH at 50 °C, Sigma Aldrich, St. Louis, MO, USA) (Greenspan, 1977) saturated solution and distilled water, respectively. Samples from each storage condition were collected at different time for analysis: every day during the first week, 3 times a week during the second week, and then 2 times a week. To reduce the impact of the time between sampling and experiments, the film samples were stored at −30 °C before analyses.

2.3. Physical and chemical characterizations

Selected physical and chemical properties were followed for PLA samples stored under the three different ageing conditions.

2.3.1. Film appearance

The modifications in the appearance and opacity were assessed during sampling. Images of films at different storage conditions and times were acquired using the camera (12 MPixels) of an iPhone SE (Apple, Cupertino, CA, USA).

2.3.2. Microstructure analysis

The microstructure of both surface and cross-section of PLA was assessed by Scanning Electron Microscopy (SEM) analysis. Images were collected using a JSM-7600F scanning electron microscope (JEOL USA Inc., Peabody, MA, USA) with 1 kV as accelerated voltage of observation, 9×10^{-6} Pa for the vacuum and lower detector (LEI) as secondary electron detector.

2.3.3. Surface hydrophobicity

The surface hydrophobicity was determined using water contact angle measurements by goniometry. A water drop (≈1 μL) was deposited on the film surface and the contact angle was measured using a goniometer (Drop Shape Analyser 30, Krüss GmbH, Hamburg, Germany) equipped with an image analysis software (ADVANCE – Drop Shape, version 1.4.2, KRÜSS GmbH). Five replicates were performed for each tested sample.

2.3.4. Molecular weight distribution

The molecular weight distribution of PLA samples was analysed over time by Size-Exclusion Chromatography (SEC), using a 1260 Infinity liquid chromatography system (Agilent Technologies, Santa Clara, CA, USA). It was composed of 2 Polypore Size Exclusion columns (Agilent Technologies, Santa Clara, CA, USA) connected in series. PLA samples (≈50 mg) were placed in 10 mL vials, 1 mL of