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Migration kinetics of sorbic acid from polylactic acid and seaweed based films into food simulants

A.V. Rodríguez-Martínez [a], R. Sendón [a], M.J. Abad [b], M.V. González-Rodríguez [b], J. Barros-Velázquez [c], S.P. Aubourg [d], P. Paseiro-Losada [a], A. Rodríguez-Bernaldo de Quirós [a, *]

[a] Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Pharmacy, University of Santiago de Compostela, E-15782, Spain
[b] Grupo de Polímeros, Universidad de A Coruña, CIT, Campus de Esteiro, s/n, 15403 Ferrol, Spain
[c] Department of Analytical Chemistry, Nutrition and Food Science, School of Veterinary Sciences, University of Santiago de Compostela, Lugo, Spain
[d] Department of Food Science and Technology, Marine Research Institute (CSIC), Vigo 28, Spain

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Active antimicrobial films based on biodegradable materials are now widely used for food packaging applications.

In the present study, an extrusion process was used to prepare biodegradable films based on polylactic acid PLA and supplemented with sorbic acid and seaweeds (PLA + 0.5% sorbic acid; PLA + 0.5% sorbic acid + 8% seaweed).

The kinetics of sorbic acid migration from the films into two food simulants (10% ethanol [v/v] and 95% ethanol [v/v]) were analysed at 5, 20 and 40 °C. The sorbic acid content in the food simulants was determined by reversed-phase high-performance liquid chromatography (detection wavelength, 260 nm). Separation was performed on a reversed-phase C18 column, at 30 °C. The diffusion coefficients were calculated using a mathematical model based on Fick's Second Law. The values obtained ranged between 4.11×10^{-9} and 1.00×10^{-13} $cm^2\ s^{-1}$.

The developed active films could be of great interest for food industry, since they could be useful for protecting packed food.

1. Introduction

In recent years, research on packaging systems has focused on the so-called active and intelligent packaging. Such packaging is designed to interact with the food product and prolong its shelf life (active packaging) or to monitor and provide information regarding the state or handling conditions to which the food has been submitted (intelligent packaging). Some active packaging systems contain compounds such as antioxidants and antimicrobial agents that are subsequently released to perform their function.

Consumers are now demanding the use of safer and more natural ingredients in food packaging. Thus, sorbic acid is increasingly used, in preference to other preservative agents, because of its safety and low physiological influence on organoleptic characteristics (Hauser & Wunderlich, 2011). Sorbic acid has been widely used as food preservative, it is classified as GRAS additive and it is effective against yeast and moulds but only partly inhibits bacterial growth (Davidson, Jueja, & Branen, 2001; Guillard, Issoupov, Redl, & Gontard, 2009). This antimicrobial agent has been successfully used in different active systems. In a study carried out to test how well antimicrobial films, enriched with sorbic acid, conserved pastry dough, the active films proved be effective in controlling microbial growth (Silveira et al., 2007a).

Modified silica films containing biocides, including sorbic acid, have shown the inhibition of the growth of *Escherichia coli*, *Lactobacillus plantarum* and *Penicillium* spp. (Böttcher, Jagota, Trepte, Kallies, & Haufe, 1999).

Inclusion of sorbic acid is permitted in a wide variety of products, such as cakes, fruit juice, jam, butter, wines, pickles, salad cream and fresh packed salad. Because of its low dissociation constant, sorbic acid can also be added to acidic and slightly acidic food (maximum pH 6.5) (Davidson et al., 2001).

* Corresponding author.
E-mail address: ana.rodriguez.bernaldo@usc.es (A. Rodríguez-Bernaldo de Quirós).

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There are three types of seaweeds: red, brown and green. Seaweeds are considered an excellent source of biologically active substances such as polysaccharides, proteins, lipids, minerals, carotenoids, vitamins, ω3 fatty and polyphenols among others (Kumar, Ganesan, Suresh, & Bhaskar, 2008; Plaza, Cifuentes, & Ibáñez, 2008). So the macroalgae themselves can be incorporated as active ingredient in different matrix (e.g. PLA, etc.) to develop an active food packaging.

Importantly, seaweeds are easy to cultivate, grow rapidly and the production of some active compounds can be controlled by modifying the culture conditions (Plaza et al., 2008).

There is also growing interest in making packaging from biodegradable materials. This interest is partly due to the environmental and economical implications of the use of materials made from petrochemical derivatives (to date the materials most commonly used), and partly to social pressure from consumers who are demanding more natural and environmentally friendly products (Janjarasskul & Krochta, 2010).

Petrochemical-based films are discarded once their function is complete. They are disposed of in landfill sites where they persist forever because they are not biodegradable. Moreover, suitable sites for landfills are increasingly difficult to find. Recycling could be a solution to reduce residues. But however in many cases when packaging materials are contaminated with biological compounds the recycling process is unfeasible and economically not suitable (Siracusa, Rocculi, Romani, & Dalla Rosa, 2008).

The increasing price of petroleum may also hamper production of such films in the near future.

Finally, social demand is an important driver for the development of biodegradable packaging. Special emphasis is now being placed on producing films that are free from toxicity risks associated with the components or migration of undesirable substances to the food (Jamshidian, Tehrany, Imran, Jacquot, & Desobry, 2010). Several biodegradable materials have been tested, with satisfactory results, with the aim of improving the quality and safety of food products; however, these are not yet widely used in the industry because of their high cost, low yield, and difficulties in fabrication (Mensitieri et al. 2011).

This is the case with polylactic acid (PLA) based films. Polylactic acid is a biopolymer that is chemically synthesized from the lactic acid obtained by fermentation of renewable sources such as corn, beets, wheat and other starchy products. Other biodegradable materials such as chitosan have also been widely used in the development of active food packaging (Lago et al. 2014).

The safety of PLA as a food contact polymer has been assessed under different conditions by studying the migration of the most probable agents (lactic acid monomers, dimmers and oligomers), following guidelines issued by the US Food and Drug Administration; the authors of the study concluded that PLA is safe and classified it as GRAS (Generally Recognized as Safe) for food contact use (Conn et al., 1995).

Polylactic acid based films show similarities to petrochemical-based films in many mechanical properties: traction resistance, resistance to UV and fatty products, low temperature sealing and resistance to odours (Cutter, 2006); however, other characteristics, such as barrier and heat sealing properties, must be improved. The current challenge is therefore to improve these films by changing some aspects of the fabrication process, such as the optical isomer composition and copolymerization with other compounds (Mensitieri et al. 2011).

Different food active packaging systems based on PLA have recently been reported, e.g. extruded PLA-based acid films containing synthetic phenolic antioxidants (Jamshidian, Tehrany, & Desobry, 2012). The same authors also prepared solvent-cast PLA films containing ascorbyl palmitate, butylated hydroxyanisole, butylated hydroxytoluene, propyl gallate, tertbutylhydroquinone and α-tocopherol as active compounds (Jamshidian, Tehrany, & Desobry, 2013).

In the present study, two biodegradable/compostable PLA-based films were developed. Sorbic acid (SA) (E-200) was incorporated in both films, and seaweeds (genus *Fucus*) only in one of the films. *Fucus* was selected because its remarkable antimicrobial activity in a preliminary screening study in which other four seaweeds were included. An extraction method for sorbic acid, and a method of analysis by HPLC to enable assessment of the films, were optimized. Finally, the kinetics of migration of sorbic acid from the mentioned films into food simulants were studied.

2. Materials and methods

2.1. Chemical and reagents

Commercial polylactic acid, Bio-Flex® F 6510, (FKuR Kunststoff GmbH, Germany) with a melt flow index (MFI) of 4.3 (±0.2) g $\times 10^{-1}$ min^{-1} (190 °C, 2.16 kg) and a density of 1.29 (±0.01) g cm^{-3} was used in the study.

Sorbic acid of purity >99% (CAS Nº: 110-44-1) and acetic acid (HPLC grade) were purchased from Sigma–Aldrich. Ethanol (analytical grade) and methanol (HPLC grade) were provided by Merck. The water used to prepare all solutions was purified in a Milli-Q water purification system (Millipore) (Bedford, MA, USA).

2.2. Seaweed samples

Fucus spiralis and other four seaweed species belonging to the genera *Bifurcaria, Gracilaria, Ulva* and *Ascophyllum* were initially tested. Supernatants from 20% w/v ethanolic extracts from the five seaweeds were prepared and tested for antimicrobial activity against *Bacillus cereus, Bacillus subtilis, Staphylococcus aureus, Klebsiella pneumoniae, Pseudomonas fluorescens, E. coli, Aeromonas hydrophyla, Vibrio alginolyticus* and *Vibrio parahaemolyticus* by means of plate bioassays (data not shown). *F. spiralis* was selected as it was found to exert the most intense antimicrobial activity against the above-mentioned indicator strains.

Dried and pulverized seaweed of the genus *Fucus* were kindly provided by the Portomuiños seaweed manufacturing company (A Coruña, Spain). Seaweeds were collected from the Atlantic coastal region of Galicia (NW Spain).

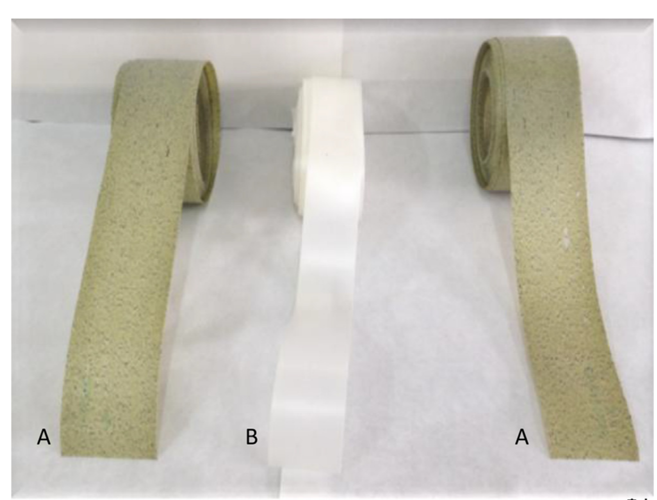

Fig. 1. Photograph of films comprising PLA + *Fucus* + sorbic acid (A) and PLA + sorbic acid (B) produced by extrusion.