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Cross-linked methyl cellulose films with murta fruit extract for antioxidant and antimicrobial active food packaging

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2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonate) (ABTS) (PubChem CID, 90658258)
Polyethylene glycol (PubChem CID, 24762)
glutaraldehyde (PubChem CID, 3485)
Gallic acid (PubChem CID, 370)
Trolox (PubChem CID, 40634)
Folin-Ciocalteús phenol reagent (PubChem CID, 516996)
Anhydrous sodium carbonate (PubChem CID, 10340)

A B S T R A C T

The use of biopolymers as substitutes for non-degradable traditional plastics is an interesting alternative particularly for short-term applications, such as food packaging. Additionally, active packaging has attracted much attention as an innovative technology for food conservation. Thus, the functionality of biocomposite films based on methyl cellulose (MC) and murta fruit (MU) (*Ugni molinae* Turcz) extract was studied. Murta fruit is a native Chilean berry and good source of antioxidant and antimicrobial compounds. First, a MU extract with the highest antioxidant ability and polyphenolic content was selected, and active MC films were prepared by casting using glutaraldehyde (GA) to improve their water resistance. The effects of GA concentration and incorporation of MU extract on material properties and antimicrobial and antioxidant activities were examined. The addition of GA greatly decreased swelling index, improved mechanical properties and antioxidant and antimicrobial activities achieved highest potential when GA was added at lowest concentration.

1. Introduction

During the last years, the research on the development of active materials with antimicrobial and antioxidant properties has increased enormously with the purpose to protect food from oxidative reactions and microbial growth. Furthermore, the application of natural ingredients is a new trend in the food industry and food research, i.e., natural preservatives derived from natural sources, instead of synthetic substances and the reduction of additives in foods. Natural substances such as α-tocopherol, essential oils and plant extracts have been incorporated into polymers for the preparation of active packages (Galotto, Guarda, & Lopez de Dicastillo, 2015; GómezEstaca, Lopez de Dicastillo, Hernandez Muñoz, Catala, & Gavara, 2014). On the other hand, the production and the use of plastics throughout the world have grown enormously, worsening environmental impact and problems of the waste disposal. The use of biopolymers as substitutes for non-degradable synthetic polymers is becoming a sustainable alternative, particularly interesting for short-term applications, such as food packaging. Thus, the development of biodegradable active packaging containing natural extracts derived from plants is one interesting strategy largely considered by the food packaging industry (Cooper, 2013; Seydim & Sarikus, 2006; Song, Lee, Al-Mijan, & Song, 2014). One alternative to develop bio-based materials is by film coating multilayer. A film coating is a thin polymer-based coat between 20 and 10 μm applied to a solid support. Biobased coatings

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offer extra advantages such as low costs due to the reduction on amount of polymer, reducing terms of CO_2 emissions, and the processing temperatures are lower, which is very useful to avoid thermal degradation of active agents. For industrial processes, the techniques can be extrusion or co-extrusion for multilayer films, lamination, and mainly roll-drying for the solvent removal of the polymer solution (Debeaufort, Quezada-Gallo, & Voilley, 1998; Vartianinen, Vaha-Nissi, M., & Harlin, 2014).

Among the biopolymers, anionic linear polysaccharides derived from cellulose, such as methyl cellulose (MC), are very promising because they are environmentally friendly due to their biodegradability. In the food industry, MC films promise important potential to be used for packaging applications due to their excellent film-making properties, large availability, low cost, transparency, high-strength and easy ability to be processed (Aminabhavi, Balundgi, & Cassidy, 2008; Cooper, 2013; Rimdusit, Jingjid, Damrongsakkul, Tiptipakorn, & Takeichi, 2008). Methyl cellulose are polysaccharides composed of linear chains of β(1 → 4) glucosidic units with methyl substituents that provides films that are water soluble and oil-and grease resistant and with efficient oxygen and lipid barrier properties (García, Pinotti, Martino, & Zaritzky, 2004; Nisperos-Carriedo, 1994; Park & Ruckenstein, 2001).

MC films, like most films based on biopolymers, are highly sensitive to environmental conditions and due to their hydrophilic nature, physical properties are very susceptible to moisture and biodegradability. As a result, several researchers have developed new formulations through small chemical modifications of these polymers, such as crosslinking processes which promote covalent linkages between polymer chains. Crosslinking is one of the most popular methods used to modify water-soluble polymers in order to achieve desired properties. MC can be cross-linked by means of different methods, such as radiation or by using convenient chemical cross-linkers consisting on aldehydes, polyepoxy compounds, and even tea catechins (Atala, 2002; Wach, Mitomo, Nagasawa, & Yoshii, 2003; Yu, Tsai, Lin, Lin, & Mi, 2015).

Glutaraldehyde, GA, is a widely used cross-linker which forms a strong covalent attachment onto a polymer surface, providing the way for a rigid structure (Hernández-Muñoz, Villalobos, & Chiralt, 2004; Lee et al., 2005; Mansur, Sadahira, Souza, & Mansur, 2008; Park, Bae, & Rhee, 2000). Some polymer characteristics could be altered by crosslinking such as permeability, mechanical properties and drug releasing. The effect of addition of cross-linkers on compounds that are desired to be released has been already studied, but mainly with pharmaceutical applications (Aiedeh, Taha, Al-Hiari, Bustanji, & Alkhatib, 2006; Ranjha & Qureshi, 2014; López de Dicastillo, Jordá, Catalá, Gavara, & Hernández, 2011; Martinez, Caves, Ravi, Li, & Chaikof, 2014; Teng, Cappello, & Wu, 2011).

In the development of active materials it is important to reach a controlled release of active components to the food to protect it from oxidation or microbial spoilage, enhancing food safety and shelf life. In this work, the effect of crosslinking on the release of antioxidant compounds from active packaging was evaluated. Release of these active agents will be completely dependent on the swelling degree of the polymer. Due to its hydrophillicity, methyl cellulose was chosen in this work to be the polymer matrix in the development of active materials for food packaging systems (Calatayud et al., 2013; Lopez de Dicastillo, Nerin et al., 2011). On the other hand, GA was selected as cross-linker agent due to its proven effectiveness in other works and to avoid degradation of phenolic compounds propitiated by irradiation (Beaulieu, D'Aprano, & Lacroix, 1999, Hirashima et al., 2013, Park & Ruckenstein, 2001; Rimdusit et al., 2008). And finally, polyethylene glycol was incorporated as plasticizer. The use of plasticizer is very important on the materials development with biodegradable polymers because they decrease the intermolecular interactions among the functional groups of the backbone chains, resulting in increased flexibility and extensibility. In food industry, polyethylene glycol (PEG) has been widely used for MC products for rolling, casting, or extruding processes because it provides several advantages due to chemical interactions between MC and PEG structures (Park & Ruckenstein, 2001; Sarkar & Walker, 1995).

Ugni Molinae, also known as "murta", "murtilla", "uñi" or "Chilean cranberry", is a native plant from Chile, western Argentina, and certain regions of Bolivia. It is a wild shrub of the Myrtaceae family that bears aromatic red globular fruit that is said to combine the sweetness of a strawberry with the pungency of a guava and the texture of a dried blueberry. Previous studies have shown murta fruit is composed by high levels of flavan-3-ols, such as catechin and epicatechin, flavonols, such as quercetin and quercetin-3-glucoside, and hydroxycinnamic acid, such as caffeic acid-3-glucoside. The other compounds were anthocyanins, like cyanidin-3-glucoside and peonidin-3-glusocide, rutin, gallic acid, quercitrin, luteolin, kaempferol, p-coumaric and myricetin, that could afford interesting antimicrobial and antioxidant activities for food protection (Alfaro et al., 2013; Junqueira-Gonçalves et al., 2015; Ruiz et al., 2010; Schreckinger, Lotton, Lila, & Gonzalez de Mejia, 2010).

2. Materials and methods

2.1. Materials and reagents

Methyl cellulose (MC) was obtained from Reutter S. L. (Santiago, Chile), 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonate) (ABTS), Folin Ciocalteu phenol reagent, anhydrous sodium carbonate, Gallic acid, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) and polyethylene glycol (PEG) (average molecular weight 190–210) were purchased from Sigma Aldrich Quimica S.A. *Ugni Molinae* fruit, commonly known as murta berry fruit, MU, was obtained from "NativforLife", an USDA and IMO organic grade certified company, whose fruits were already dried and milled.

Gram-positive bacteria *Listeria innocua* ATCC33090 was obtained from Laboratory Microbiologics (University of Chile, Chile) and stored in Tryptone soy broth (TSB) at −80 °C until needed. For experimental use, the stock cultures were maintained on Tryptone soy agar (TSA) slants at 4 °C, and for experimentation, a loopful of each strain was transferred to 10 mL of TSB and incubated at 37 °C for 18 h to obtain fresh early-stationary phase cells.

2.2. Native fruit studies—antioxidant activity and polyphenolic content

Murta fruit powder was extracted under ethanol, ethanol 50% and distilled water in order to study the polarity of the most antioxidant compounds and find the extract with highest antioxidant capacity. The extraction was carried out at 40 °C during 3 h in an Erlenmeyer flask in a shaking incubator at 150 rpm. Then the mixtures were centrifuged and the upper phases were evaluated through ABTS method and Folin Ciocalteu test in order to measure antioxidant capacity (as radical scavenging capacity) and polyphenolic content, respectively. Folin-Ciocalteu method was done according to the method of Singleton, Orthofer, & Lamuela-Raventós, 1999, with some modifications (Singleton et al., 1999). Gallic acid was used as the standard for the calibration curve and polyphenol content (PC) was expressed as gallic acid equivalents (GA).

ABTS method was done according to previous works (Lopez de Dicastillo, Castro-Lopez, Lasagabaster, Lopez-Viariño, & Gonzalez-Rodriguez, 2013). ABTS assay is based on the inhibition of the radical cation 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonate),