Food Packaging and Shelf Life 18 (2018) 42–50

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

journal homepage: www.elsevier.com/locate/fpsl

Release kinetics of rosemary (*Rosmarinus officinalis*) polyphenols from polyvinyl alcohol (PVA) electrospun nanofibers in several food simulants

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ARTICLE INFO

Keywords:
Active packaging
PVA
Rosemary
Electrospinning
Release kinetics
Food simulants

ABSTRACT

Polyvinyl alcohol (PVA) electrospun mats with antioxidant activity (PVA/Ros) were obtained by incorporating rosemary extract (RE) into the electrospinning precursor solution. RE compounds interact with PVA, favoring the retention of polyphenols (88 ± 2%), and improving its thermal stability. The components extracted from PVA/Ros mat were the same as those of the RE. PVA/Ros mats showed a polyphenol content of (15.4 ± 0.5) mg gallic acid equivalent/g of mat (mg GAE/g) and achieved an antioxidant activity of (120 ± 8) μmoles Trolox equivalent/g of mat (μmol TE/g), as measured by Folin-Ciocalteu method and DPPH· assay. The release rate of rosemary polyphenols to several food simulants was measured and kinetic data was adjusted by Fick's diffusion law, Power Law, and Weibull model. The resulting parameters suggested that polymer chain relaxation is the leading mechanism in hydrophilic simulant, while an anomalous release occurred in acid medium. A burst release was observed in lipophilic food simulant, limiting its effectiveness over time. This work shows the potential application of PVA/Ros mats as active food packaging, particularly for hydrophilic and acid food products.

1. Introduction

A new trend in the food packaging industry is the incorporation of bioactive natural components in the packaging material, in order to preserve food quality and extend its shelf life. In particular, the addition of antioxidant natural plant extracts to food packaging avoids oxidative damage during storage. The availability of bioactive compounds can be increased if the packaging material surface is designed as a nanostructure, due to its higher surface to volume ratio with respect to a bulk material. Additionally, the nanostructure could influence the release rate of these compounds (Wen, Zong, Linhardt, Feng, & Wu, 2017). A very promising technology to produce nanostructured materials for food packaging containing different active components is the electrospinning technique (Jacobsen, Garcia-Moreno, Mendes, Mateiu, & Chronakis, 2018).

Recently, it was demonstrated that rosemary extract is a very effective "green" antioxidant for food (Bonilla, Sobral, & do, 2017; López-Córdoba, Medina-Jaramillo, Piñeros-Hernandez, & Goyanes, 2017). Rosemary (*Rosmarinus officinalis*) leaves are an important source of antioxidant molecules, including phenolic compounds and diterpenes. They are commonly used to prepare different rosemary extracts or rosemary essential oils for various applications (Ho et al., 1998; Tu, Moss-Pierce, Ford, & Jiang, 2013; Urbančič, Kolar, Dimitrijević, Demšar, & Vidrih, 2014; Yang et al., 2016). Some authors have reported that rosemary extract composition depends on which solvent and extraction techniques are employed (Carvalho, Moura, Rosa, & Meireles, 2005; Herrero, Plaza, Cifuentes, & Ibáñez, 2010; Ibanez et al., 2003; Moreno, Scheyer, Romano, & Vojnov, 2006). Among the numerous compounds extracted from rosemary leaves, antioxidant activity is mainly attributed to rosemarinic acid, carnosic acid and carnosol content.

Rosemary extracts have previously been incorporated into different polymeric films to produce a potential active packaging. For example, Gómez-Estaca, Bravo, Gómez-Guillén, Alemán, and Montero (2009) studied antioxidant activity of gelatin-based films with the addition of aqueous rosemary extract, showing that the source of gelatin considerably affected the release of polyphenols due to different molecular interactions; Farghal, Karabagias, El Sayed, and Kontominas (2017) have coated polyethylene terephthalate commercial films with rosemary extract in order to protect fish from oxidation; Piñeros-Hernandez, Medina-Jaramillo, López-Córdoba, and Goyanes (2017)

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https://doi.org/10.1016/j.fpsl.2018.08.006
Received 14 March 2018; Received in revised form 12 June 2018; Accepted 13 August 2018
2214-2894/ Published by Elsevier Ltd.

incorporated rosemary aqueous extract in casting cassava starch films; and López-Córdoba et al. (2017) reported that the incorporation of rosemary ethanolic extract in starch filmogenic solution led to the formation of dispersed nanoparticles containing the extract active principles. The formation of nanoparticles was a consequence of the solvent displacement phenomenon. Solvent displacement occurs when the solute solution is incorporated into another solvent (normally referred as anti-solvent) in which the solute is poorly soluble. This incorporation leads to a supersaturation state, which is the driving force for nanoparticle formation (Joye & McClements, 2013).

Nevertheless, there are few studies regarding the incorporation of rosemary extract to electrospun mats. Colín-Orozco, Zapata-Torres, Rodríguez-Gattorno, and Pedroza-Islas (2015) have electrospun whey protein isolate/poly (ethylene oxide) with the addition of rosemary extract, and have studied the dependence of the rosemary release rate on the pH of the medium. Electrospinning is a well-established and scalable technique that allows the production of nanofibers with the capability to entrap and deliver different molecules (Celebioglu & Uyar, 2017; Celebioglu, Yildiz, & Uyar, 2018; Echegoyen, Fabra, Castro-Mayorga, Cherpinski, & Lagaron, 2017; Mujica-Garcia et al., 2016; Ribba, Parisi, D'accorso, & Goyanes, 2014). The use of electrospinning mats could change the release kinetics of active components compared to continuous films, due to the high surface to volume ratio of the mat nanofibers.

Poly(vinyl alcohol) (PVA) is an electrospinable, biodegradable (DeMerlis & Schoneker, 2003), water soluble, and non-toxic polymer permitted for use in food contact materials by the U.S. Food and Drug Administration (US Food & Drug Administration, 2003a, 2017), with a recommended maximum edible dose of 3 mg/kg body weight/day (US Food & Drug Administration, 2003b). PVA electrospun mats have been used by many authors to encapsulate different natural active molecules and extracts, including geraniol, vanillin, cinnamaldehyde, eugenol, d-limonene, and aloe vera, among others (Camerlo, Vebert-Nardin, Rossi, & Popa, 2013; Echegoyen et al., 2017; Kayaci & Uyar, 2012; Kayaci, Ertas, & Uyar, 2013; Kayaci, Sen, Durgun, & Uyar, 2014; Lemma et al., 2015; Torres-Giner, Wilkanowicz, Melendez-Rodriguez, & Lagaron, 2017; Wen et al., 2016). Reticulating PVA with an edible agent reduces PVA water solubility -one of the main limitations for its use as a controlled release system in aqueous mediums- without losing its potential application in food industry. Recently López-Córdoba, Castro, and Goyanes (2016) showed that citric acid (CA) crosslinking improves water stability of PVA mats, and consequently they obtained a controlled release system for tetracycline hydrochloride.

To the best of our knowledge, there are no reports about the release kinetics of rosemary polyphenols in different food simulant mediums from PVA electrospun mats containing rosemary extract. In this work the incorporation of rosemary extract into a crosslinked PVA electrospun mat in order to obtain an active material with controlled release capability was reported. First, a rosemary extract was obtained by solvent extraction in an ethanol:water solution (70:30 v/v) and was characterized by measuring polyphenol content and antioxidant activity. The resulting rosemary extract was incorporated into a PVA aqueous solution and electrospun. The incorporation efficiency of rosemary polyphenols and the antioxidant activity of electrospun PVA active mats were measured. Bioactive components of the original rosemary extract were compared to those present in the PVA mats containing rosemary extract and to those released from the mat in hydrophilic, lipophilic and acid food simulants. Morphological, thermal and chemical characterizations were performed in order to understand the obtained results. Finally, rosemary polyphenols release kinetics was studied in several food simulants and modeled according to Fick's diffusion law, Power Law model, and Weibull model in order to elucidate mechanisms involved in its release.

2. Experimental

2.1. Materials

Polyvinyl alcohol Mowiol 10–98 (Mw = 61000, Sigma-Aldrich, Germany), citric acid (Stantom, Argentina), Folin-Ciocalteu reagent (Anedra, Argentina), DPPH· reagent (Sigma-Aldrich, Germany), gallic acid (Anhydrous p.a., Biopack, Argentina), and Trolox (Sigma-Aldrich, Germany) were used as received. Rosemary dried leaves were purchased in a local trade; distilled water and food grade ethanol (96% v/v) were used.

2.2. Rosemary extract

Extraction was performed according to the procedure recently optimized by Oliveira, Oliveira, Conceição, and Leles (2016). Briefly, 10 g of dried rosemary leaves were milled and dispersed in 50 mL of ethanol:water solution (70:30 v/v). The mixture was placed in a thermostatic bath at 50 °C for 55 min. The obtained rosemary extract was cooled at room temperature and filtered (pore size 0.8 μm). The resulting solution was named RE; it was clear and without any precipitates. The extraction yield was determined gravimetrically, by drying 5 mL of RE at 50 °C until constant weight. The yield was (59 ± 1) g of dried solids extract/L of RE. The obtained rosemary powder was characterized by FTIR and TGA measurements. These experiments were performed on the powder instead of RE in order to avoid interferences from the solvent and interactions between solvent and rosemary compounds.

The total polyphenols content of RE was determined by Folin Ciocalteu method (Singleton, Orthofer, & Lamuela-Raventós, 1999). Briefly, 400 μL of each sample were mixed with 2 mL of Folin-Ciocalteu reagent (1:10 diluted). Then, 1.6 mL of sodium carbonate (7 g/100 mL) were added to each sample. Absorbance was measured at 760 nm after 30 min reaction using a spectrophotometer (SHIMADZU UV-1800, Japan). Calibration curve was obtained using gallic acid (Biopack, Argentine) as a standard, in a range between 10 mg/L and 150 mg/L. Results were expressed as gallic acid equivalents (GAE/mL of RE).

Antioxidant activity of RE was measured using 1,1-diphenyl-2-picrylhydrazyl (DPPH·) reagent as a free radical (Brand-Williams, Cuvelier, & Berset, 1995). RE was diluted in order to achieve different antioxidant concentrations. Then, 100 μL of each dilution were mixed with 3.9 mL of DPPH· in methanol (25 mg/L). Absorbance was measured at 516 nm after 30 min reaction. The DPPH· scavenging activity is defined by:

$$DPPH \quad inhibition\,(\%) = 100.\frac{A_b - A_s}{A_b}, \tag{1}$$

where A_b is the absorbance of the blank and A_s is the absorbance of the sample. Antiradical activity was first expressed as the amount of antioxidant necessary to decrease the initial DPPH· concentration by 50%, called efficient concentration (EC_{50}) (Brand-Williams et al., 1995). Inhibition of DPPH free radicals was compared with a Trolox calibration curve (5–40 mM), and antioxidant activity was also expressed as μmol Trolox equivalent (TE)/mL of extract (Delgado, Galleano, Añón, & Tironi, 2015).

2.3. Electrospinning process

PVA electrospun solution was obtained by dissolving 12 g of powdered PVA with 0.6 g of citric acid (5% w/w respect to polymer) in 88 mL of distilled water, at 80 °C for 1 h under constant magnetic stirring (PVA*). In the case of the sample containing RE (PVA/Ros), 20 mL of water were replaced by 20 mL of the extract, which was added dropwise under constant stirring and then mixed for 30 min. PVA solution became turbid after RE addition, suggesting the formation of particles as a consequence of solvent displacement phenomenon. In

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