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Characterization of ethylene-vinyl alcohol copolymer containing lauril arginate (LAE) as material for active antimicrobial food packaging

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ABSTRACT

The aim of this work was to characterize, as packaging materials, antimicrobial films based on two different ethylene vinyl alcohol copolymers (EVOH 29 and EVOH 44) containing 5 and 10% lauril arginate (LAE). The characterization included optical, surface, thermal and barrier properties of the developed films, as well as the release of the agent into aqueous media. The results show that the addition of LAE did not produce relevant changes in optical, but reduced the films' barrier properties to oxygen and water vapor, especially at high humidity conditions, and improved the wettability of the surface as demonstrated by the significant decrease in contact angle, both effects a consequence of the surfactant properties of the compound. The thermal properties confirmed that the distribution of LAE in the matrix was homogeneous, that the agent induced an antiplasticization effect and reduced the quality and percentage of the crystalline region, and that casting (or coating) is a suitable processing technology to reduce compound degradation. Finally, the release of LAE from EVOH films to water was characterized at 4 °C and 23 °C. This study showed that the agent was fully released into the food simulant from all films, although kinetically LAE diffusion was faster in EVOH 29 and at higher temperature. All these results show that the developed films present excellent functional properties and are able to release the antimicrobial agents suitably, making them promising materials for active food packaging applications.

1. Introduction

Active antimicrobial packaging has received special attention in the last years since they are one of the most promising packaging alternatives in the use of less aggressive emerging food technologies. Antimicrobial packaging extends the shelf life of sensitive product by inhibiting or retarding the proliferation of microorganisms in food (Appendini & Hotchkiss, 2002). To avoid the risk of consumer manipulation of the active compounds, the addition of the agent within the packaging walls, that is, into the polymeric matrix that constitutes the packaging wall or onto the inner surface are the preferred incorporation methods. Diverse polymers have been studied as possible matrices for the incorporation of antimicrobial agents including biopolymers and synthetic polymers.

In a previous work (Muriel-Galet, Lopez-Carballo, Gavara, & Hernandez-Munoz, 2012), two different ethylene-vinyl alcohol copolymers (EVOH 29 and EVOH 44) were used as matrices to incorporate the antimicrobial agent lauril arginate (LAE) and the results showed that the films presented excellent antimicrobial activity.

EVOH copolymers are common packaging materials classified as biodegradable and biocompatible (Oyane, Uchida, Onuma, & Ito, 2006) that present excellent oxygen barrier

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properties and a highly hydrophilic nature (Aucejo, Catala, & Gavara, 2000). This latter property is highly inconvenient in applications where high barrier to oxygen is a requirement since water gain results in polymer plasticization and subsequently severe permeance increment. Recently, EVOH materials have been used as matrices for the development of active packaging systems. In these applications, water plasticization is beneficial because when the polymer is exposed to a humid environment (that is, the food packaging step) plasticization accelerates agent release, producing the expected useful effect on the food (Lopez-de-Dicastillo, Catala, Gavara, & Hernandez-Munoz, 2011; Muriel-Galet et al., 2012; Muriel-Galet, Lopez-Carballo, et al., 2012).

Lauril arginate, LAE, (95% of ethyl-N-dodecanoyl-L-arginate hydrochloride) is a cationic surfactant, a derivative of lauric acid, L-arginine, and ethanol (Ruckman, Rocabayera, Borzelleca, & Sandusky, 2004). This compound is considered one of the most potent food antimicrobial agents with an extensive spectrum of antimicrobial activity (Bakal & Diaz, 2005), and it does not provide any taste or odor, in compliance with article 3 of the European Regulation on active food packaging materials (EU, 2011). In addition, it has been classified as GRAS (Generally Recognized as Safe) and food preservative by the Food and Drug Administration (FDA).

The purpose of this study was to characterize the functional properties of antimicrobial films based on two ethylene vinyl alcohol copolymers with different vinyl alcohol content (EVOH 29 and EVOH 44) containing 5 and 10% of LAE so as to be considered suitable food packaging materials. It is known that the incorporation of agents into a polymeric matrix can modify unacceptably the engineering properties of the packaging materials (Bastarrachea, Dhawan, & Sablani, 2011). The films were developed by a procedure that resembles film coating, which is the method considered for its application in packaging design. In such designs, mainly the substrate material is responsible for mechanical strength (reason why mechanical characterization of the active EVOH films were not included in this study), although the coating can modify many other relevant properties of the final structure. Accordingly, this characterization included optical, surface, thermal and barrier properties of the developed films, relevant to being used as conventional packaging materials and full evaluation of the agent release process into aqueous media, relevant to the design of efficient active packages.

2. Materials and methods

2.1. *Materials*

Ethylene vinyl alcohol copolymers with 29% ethylene molar content (EVOH 29) and with 44% ethylene molar content (EVOH 44) were kindly provided by The Nippon Synthetic Chemical Company (Osaka, Japan). 1-Propanol was purchased from Sigma (Madrid, Spain). The antimicrobial lauril arginate ($C_{20}H_{41}N_4O_3Cl$) was provided by Vedeqsa Grupo LAMIRSA (Terrassa, Barcelona, Spain). Water was obtained from a Milli-Q Plus purification system (Millipore, Molsheim, France).

2.2. *Film preparation*

EVOH films were prepared as described elsewhere (Muriel-Galet, Lopez-Carballo, et al., 2012). Briefly, the film forming solution was prepared by dissolving the copolymers in a mixture of 1-propanol and water, 1/1 (v/v) for EVOH 29 and 2/1 (v/v) for EVOH 44. The solutions were stirred using a magnetic stirrer hotplate at 50 °C. After solution, a concentration of 5 and 10% LAE was added and stirred again for about 15 min. Control films were obtained without LAE. EVOH solutions were extended over a clean glass plate using a 200 μm deep thread spreading bar (Lin-Lab Rioja, Logroño, Spain). The films were dried in a tunnel equipped with a 2500 W heat source for 10 min. The thickness of these films was determined with a Mitutoyo micrometer (Osaka, Japan) in each film before analysis.

2.3. *Optical properties*

A Konica Minolta CM-3500d spectrophotometer (Konica Minolta Sensing, Inc., Osaka, Japan) set to D65 illuminant/10° observer was used to determine the film color. The samples were measured against the surface of a standard white plate. The instrument's software SpectraMagic NX was employed to acquire the color data and to display them in the CIELAB color space. The parameters L^* [black (0) to white (100)], a^* [green (−) to red (+)] and b^* [blue (−) to yellow (+)] were obtained and the polar coordinates, the chroma C^* and the hue angle $h°$ calculated. Eight measurements were taken of each sample, and three samples of each film were measured.

Film transparency was measured by using a Jasco V-360 spectrofotometer (Madrid, Spain) and monitoring the transmittance at 600 nm of 4.5 cm × 1.2 cm samples. Three films were analyzed per sample.

Gloss was determined according to the ISO 2470 standard. Measurement of diffuse blue reflectance factor at 457 nm and with an angle of 10° was carried out in a Konica Minolta, CM-2600d spectrophotometer (AquaTeknica, Spain). Five films were analyzed per sample.

2.4. *Contact angle*

The contact angles of control and active films were measured with an OCA 15 EC (DataPhysics Instruments, Germany) to determine the effect of the LAE incorporated into the surface wettability. A 2-μL drop of distilled water was placed on the film surface. The evolution of the droplet shape was recorded and the angle was determined after 60 s; SCA20 image analysis software was used to determine the contact angle evolution. All measurements were conducted under standard atmospheric conditions at 23 ± 1 °C and a minimum of three measurements, taken at different positions on the film, and three samples of each film were measured.

2.5. *Thermal characterization*

The glass transition (T_g) and melting point (T_m) temperatures and the melting enthalpy (ΔH_m) of the samples were determined with a DSC Model Q2000 from TA Instruments (New Castle, DE, EEUU). Film samples (ca. 7 mg) previously