Carbohydrate Polymers 136 (2016) 409–417

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Near-infrared chemical imaging and its correlation with the mechanical properties of chitosan–gelatin edible films

F. Palma[a], B. Michniak-Kohn[b], J.R. Pérez-Correa[a], E. Hernandez[c], R.J. Romañach[c], L.M. Valenzuela[a,d,*]

[a] Department of Chemical and Bioprocesses Engineering, ASIS-UC Interdisciplinary Research Program on Tasty, Safe and Healthy Foods, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, Santiago, Chile
[b] Ernest Mario School of Pharmacy, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA
[c] Department of Chemistry, University of Puerto Rico, Mayagüez Campus, Mayagüez, PR 00681, Puerto Rico
[d] Research Center for Nanotechnology and Advanced Materials "CIEN-UC", Pontificia Universidad Católica de Chile, Santiago, Chile

ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form
14 September 2015
Accepted 15 September 2015
Available online 24 September 2015

Keywords:
Hydrocolloid
Near-infrared spectroscopy
Plasticizer
Molecular interaction
Tensile strength

ABSTRACT

Plasticizers influence the physical properties of edible films by their interaction with the film-forming polymers. Using near-infrared chemical imaging, it is possible to characterize the interaction between compounds through the analysis of their relative presence throughout the film (abundance) and their variability. These parameters and standard mechanical properties were used to characterize the interaction between gelatin, chitosan and several plasticizers, pure or in binary combinations. Triacetin showed the least interaction with the polymers, while polyethylene glycol 400 and glycerol showed high interaction with them. In addition, we observed that the tensile strength of the film was well correlated with the variability of gelatin and chitosan.

1. Introduction

Edible films are thin layers of a polymer material that control the solute exchange between the matrix and the environment, thus extending the shelf life of a food (Pavlath & Orts, 2009). To achieve this, the films' polymer matrix should have the necessary physical-chemical properties for the specific food with which it will be used. Edible films can be created to have the necessary mechanical and structural properties with the use of hydrocolloid molecules, which are hydrophobic biopolymers with high molecular weight and long polymeric chains (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011). The most used compound for the manufacturing of edible films is gelatin, mainly due to its ability to form films at low temperatures (Gómez-Estaca, Gómez-Guillén, Fernández-Martín, & Montero, 2011), and chitosan, for being antibacterial, biodegradable, biocompatible, non-toxic and renewable (van den Broek, Knoop, Kappen, & Boeriu, 2015).

Edible films are made up of molecular interactions between the polymers used in the film, including covalent bonds (i.e. disulfide interactions and cross-linking) as well as ionic bonds, hydrogen bonds and electrostatic interactions. These interactions generate films that are rigid and brittle, providing less protection to the food (Cao, Yang, & Fu, 2009; Rivero, García, & Pinotti, 2010). It is possible to improve the stability and performance of the edible films with the addition of plasticizers (Talja, Helén, Roos, & Jouppila, 2008). Plasticizers are compounds that reduce inter-molecular forces and increase the mobility of the polymeric chains of the film (Sothornvit & Krochta, 2005). The plasticizers interact with the polymers of the matrix through van der Waals forces, hydrogen bonds and weak electrostatic interactions (Marcilla, García, & Beltrán, 2012). The amount of oxygen atoms per molecule, the molecular weight and polarity (dielectric constant) are the characteristics of the plasticizer that determine the type and level of interaction with the film-forming polymers (Immergut & Mark, 1965). Also, the

* Corresponding author at: Pontificia Universidad Católica de Chile, Chemical and Bioprocesses Engineering, Vicuña Mackenna 4860, Macul, Santiago, Chile. Tel.: +56 2 2354 1227.
E-mail addresses: fvpalma@uc.cl (F. Palma), michniak@dls.rutgers.edu (B. Michniak-Kohn), perez@ing.puc.cl (J.R. Pérez-Correa), eduardo.hernandez1@upr.edu (E. Hernandez), rodolfoj.romanach@upr.edu (R.J. Romañach), lvalenzr@ing.puc.cl (L.M. Valenzuela).

http://dx.doi.org/10.1016/j.carbpol.2015.09.051
0144-8617/

addition of high concentrations of hydrophilic plasticizers (i.e., over 20% in chitosan films, Suyatma, Tighzert, & Copinet, 2005) could over-plasticize the films, producing phase separation (Arvanitoyannis, Nakayamab, & Aibab, 1998). Over-plasticized films are sticky, weak and extend more than required. Sometimes exudate drops can be observed in the surface of over-plasticized films (Taylor, Taylor, Belton, & Minnaar, 2009; Wilson, 1995).

Infrared spectroscopy (IR) is a good option to study the chemical interaction between compounds (Lefevre & Subirade, 2001). IR spectroscopy provides information about the internal chemical structure of the sample, for instance, the type or quantity of a given bond that is present in the sample (Zapf, 2009). This is achieved by detecting chemical bonds through the rotation and vibration that they show in a given spectral range of the electromagnetic spectrum (13,000–10 cm^{-1} or 0.76–1000 μm, depending on the units used) (Gendrin, Roggo, & Collet, 2008). One type of IR is near-infrared spectroscopy (NIR), used mainly to study the overtones and combinations of CH, OH, NH bands and stretching, as well as bond vibration modes that provide highly specific molecular information for species identification (Furukawa, Sato, Shinzawa, Noda, & Ochiai, 2007).

Near-infrared chemical imaging (NIR-CI) techniques apply conventional near-infrared spectroscopy, together with a system that captures multiple images through many wavelengths. The resulting image is a tri-dimensional (3D) matrix or hyperspectral data cube, with two spatial dimensions and one spectral dimension (Gendrin et al., 2008). The conventional NIR technique only provides the average spectrum of the surface of each sample; however, NIR-CI provides a spectrum of each pixel of the samples' entire surface, allowing a complete chemical characterization with a quick and non-invasive process.

With the information obtained by the NIR-CI, together with the use of chemometric tools, a characterization can be created with the distribution of the samples' compound of interest (Sacré et al., 2014), obtaining the histogram parameters of the compounds' intensities: mean, standard deviation, kurtosis and skew. The mean of the distribution values corresponds to the abundance of the compounds on the surface of the sample (de Juan et al., 2004). The standard deviation of the distribution is defined as the variability of the abundance of the samples' compounds (Puchert, Lochmann, Menezes, & Reich, 2010). Kurtosis measures the symmetrical tailing or 'peakedness' of the distribution, where zero indicates a normal distribution. Finally, skew is the measurement of the asymmetry of the distribution, with zero corresponding to a symmetric distribution (Lewis, Schoppelrei, Lee, & Kidder, 2007; Montgomery & Runger, 2003). Viewed together, the variability of abundance, the degree of unimodal distribution and the asymmetry of the distribution are descriptors of the homogeneity of the sample. Moreover, these parameters depend on the spectral information of the sample, which changes in response to the interaction between the components (Lefevre & Subirade, 2001).

In pharmaceutics, there are studies that relate physical properties of drug matrices with the distribution and abundance of ingredients for the NIR-CI analysis. For example, Ellison, Ennis, Hamad, and Lyon (2008) showed that NIR-CI can be an effective tool for monitoring physical quality, distribution of active pharmaceutical ingredient in the tablets, and also their uniform compaction force. Wang et al. (2014) reported correlation models that compared tablet hardness and spatial distribution, obtained using NIR-CI. Jérez Rozo et al. (2011) used NIR-CI to characterize the spatial distribution and abundance of the film-forming polymer and the drug contained in the film used in a pharmaceutical application. Both parameters were correlated with the size of the particle and the agglomeration of the drug, allowing them to determine the dissolution speed and drug uniformity obtained with the film. This suggests that the abundance and distribution of the polymeric film compounds obtained by NIR-CI, may be related to the films' physico-chemical properties.

Since the mechanical properties of edible films are determined by the interaction between the plasticizers and the film-forming polymers (Bergo & Sobral, 2007), these properties could be analyzed with NIR-CI. This paper investigates the relationship between the abundance of the compounds and their variability, as obtained with NIR-CI, and the mechanical properties of the gelatin and chitosan edible films. Our objective is to research the potential of NIR-CI to qualitatively and quantitatively characterize, in a non-invasive way, the homogeneity of the edible films and its impact on the films' mechanical properties.

Table 1
Formulation of edible films used in this study.

Compound	(g/100 g sol.)	Percentage[1]
Gelatin	2.30	46
Chitosan	1.55	31
Plasticizers[2]	1.16	23

[1] Percentage corresponds to composite grams/grams of total compounds in the film multiplied by 100.
[2] Plasticizers correspond to glycerol, sorbitol, PEG400, and triacetin, either as a single plasticizer or as a combination of two of them in a proportion 1:1.

2. Materials and methods

2.1. Materials

The film forming solutions were fabricated using gelatin from cold water fish skin (Sigma-Aldrich Lot# SLBG7701V, average molecular mass 60 kDa; bloom number: 225–325; viscosity at 24 °C, 31,500 cps), and chitosan from *Pandalus borealis* (Sigma-Aldrich Lot# MKBD4275V; medium molecular weight; 77% deacetylation, viscosity 450 mPa s at 1% concentration in 1% acetic acid). The plasticizers used were glycerol (≥99%, Sigma-Aldrich), sorbitol (≥99.5%, Sigma-Aldrich), polyethylene glycol-400 (PEG400) (EMD Millipore), and triacetin (99%, Acros Organics).

2.2. Methods

2.2.1. Film forming solutions

The film- forming solutions were fabricated by dissolving chitosan in acetic acid at 1% v/v to reach a concentration of 1.55% w/w. The dissolved chitosan was mixed with liquid state gelatin at 2.3% w/w. In each case, a plasticizer was added at 1.16% w/w (Hosseini, Rezaei, Zandi, & Ghavi, 2013), or two plasticizers at 0.58% w/w each (Table 1). Gelatin and chitosan film, without the addition of plasticizers, was used as control film. Each film-forming solution was stirred until dissolved, and then was heated and maintained at 45 °C for 1 h, being constantly stirred. The resulting solution had a pH of 4.566 ± 0.007 and was filtered using vacuum and stored at room temperature until the edible films' fabrication.

2.2.2. Fabrication of edible films

Solvent casting was used to produce edible films. Aliquots of 5.4 g of a film-forming solution were poured into petri dishes with surface areas of 24 cm^2, and dried at 30 °C and 25 ± 5% relative humidity in a system of forced air until a stable mass was reached (15 h). The average films' thickness was 100 ± 23 μm.

2.2.3. Near-infrared chemical images (NIR-CI)

A Malvern Instrument Spectral Dimension SyNIRgi spectrometer chemical imaging system (Malvern, UK) was used. The Malvern system includes a focal plan array (FPA) mode with a tunable liquid-crystal filter that allowed full field analysis.