



Effect of glycerol and corn oil on physicochemical properties of polysaccharide films – A comparative study

Miguel A. Cerqueira^{a,*}, Bartolomeu W.S. Souza^{a,b}, José A. Teixeira^a, António A. Vicente^a

^a IBB – Institute for Biotechnology and Bioengineering, Centre for Biological Engineering, University of Minho, Campus de Gualtar, 4700-035 Braga, Portugal

^b Departamento de Engenharia de Pesca, Universidade Federal do Ceará, Fortaleza - Ceará, Brazil

ARTICLE INFO

Article history:

Received 29 April 2011

Accepted 23 July 2011

Keywords:

Polysaccharide

Chitosan

Galactomannan

Edible films

Physicochemical properties

ABSTRACT

The aim of this work was to evaluate the influence of glycerol and corn oil on physicochemical properties of polysaccharide-based films. The polysaccharides used were galactomannan from *Gleditsia triacanthos* and chitosan. Fourier-transform infrared spectroscopy, differential scanning calorimetry and thermogravimetric analysis were performed, together with determinations of moisture content, solubility, water vapor permeability and mechanical properties. Structure–properties relationships were established, relating the two polysaccharides' structures with the way they interact with water, other film's constituents (glycerol and oil) and the resulting properties. The presence of glycerol and corn oil originated a more hydrophilic structure and a decreased affinity of the film matrix to water, respectively, in both polysaccharides. However, the two polysaccharides presented different behaviors in terms of glass transition temperature, water vapor permeability and elongation-at-break that have been related with the particularities of their structure: while for the galactomannan the specific sorption sites for water are the O–H groups, for chitosan those are O–H and/or NH₂ groups.

The present work provides insight regarding the physicochemical properties of polysaccharide-based films and established relationships with polymers' structure, showing that the two polysaccharides studied here have adequate properties to be used as packaging materials for specific food applications.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

In the most recent years, industries have been joining efforts to reduce the amount of synthetic materials used. Therefore research on new materials from renewable resources to be used in textile, pharmaceutical, biomedical, cosmetics and food industries has progressed in order to decrease the problem of plastic waste disposal due to lack of biodegradability (Prashanth & Tharanathan, 2007; Siracusa, Rocculi, Romani, & Rosa, 2008). In this context edible films based on polysaccharides and/or proteins appear as potential substitutes of synthetic packaging, thus playing a decisive role in the improvement of the shelf-life of food through controlling gas transfer and being carriers of functional compounds (Srinivasa, Ramesh, & Tharanathan, 2007).

Polysaccharides are natural polymers composed of mono-saccharide residues that are connected by O-glycosidic linkages and, depending on their source, they can be neutral, positively or negatively charged. They either act as energy reserve in plants and animals, or have structural roles in plant cell walls or in the tough

outer skeleton of insects and other animals (Nelson & Cox, 2000). The great diversity of structural features of polysaccharides have origin from differences in the monosaccharide composition, linkage types and patterns, chain shapes, and degree of polymerization, influencing their physicochemical properties.

Galactomannans are present in the endosperm of numerous plants, and they have several functions, e.g. as a reserve of carbohydrates. Galactomannans are polysaccharides built up of a β -(1–4)-D-mannan backbone with single D-galactose branches linked α -(1–6) (Kök, Hill, & Mitchell, 1999). Galactomannans can often be used in different forms for human consumption. Featuring different physicochemical properties, galactomannans are a versatile material used for many applications: they are excellent stiffeners and stabilizers of emulsions, and the absence of toxicity allows their use in the textile, pharmaceutical, biomedical, cosmetics and food industries (Srivastava & Kapoor, 2005). *Gleditsia triacanthos* belongs to the family *Leguminosae* and grows in America, Middle Europe and Mediterranean area (Üner & Altınkurt, 2004). Seeds of *G. triacanthos* were used as source of the galactomannan used as raw material for edible films production.

Chitosan is a natural polymer derived by deacetylation of chitin, the second most abundant biopolymer in nature after cellulose

* Corresponding author. Tel.: +351 253 604 400; fax: +351 253 604 429.

E-mail address: miguelcerqueira@deb.uminho.pt (M.A. Cerqueira).

(Shahidi, Arachchi, & Jeon, 1999). When compared with other polysaccharides, chitosan has several important advantages such as biocompatibility, biodegradability and no toxicity; several studies indicated chitosan as bacteriostatic and fungistatic (Yi et al., 2005). The polycationic properties of chitosan provide the possibility of film formation by the breakage of polymer segments and subsequent reforming of the polymer chain into a film matrix or gel; this can be achieved through the evaporation of the solvent thus creating hydrophilic and hydrogen bonding and/or electrolytic and ionic crosslinking.

Natural biopolymers present several advantages over synthetic polymers but their application is limited by their high affinity to water, leading to textural transformations that have a strong impact on their mechanical, transport and solubility properties. In a previous publication the development of edible films based in chitosan and galactomannan was discussed (Cerqueira, Lima, et al., 2009), however no relationship was established between their structure and their properties. To our knowledge no work has been published comparing the physico-chemical properties of these two polysaccharides and very few publications do it for other polysaccharides. Further, the understanding of their structure–properties relationship in order to predict and control their function is one of the major flaws in this area, especially when mixtures with other substances are considered (which is often the case). In fact, the incorporation of other compounds, such as plasticizers and lipids, is common in order to improve mechanical and transport properties of edible films (Bergo & Sobral, 2007), but research focused on e.g. polysaccharides' interaction with other film components is needed in order to understand the influence of such components in films' properties.

Plasticizers are commonly used to facilitate processing and/or to increase films flexibility. Water, oligosaccharides, polyols, and lipids are different types of plasticizers widely used in hydrocolloid-based films (Suyatma, Tighzert, Copinet, & Coma, 2005). Their combination could give rise to synergistic effects between components improving the properties of edible films. The lubrication theory postulates that plasticizers, by interspersing themselves, act as internal lubricants by reducing frictional forces between polymer chains. The gel theory postulates that the rigidity of the polymer network comes from its three-dimensional structure, and plasticizers take effect by breaking polymer–polymer interactions (e.g., hydrogen bonds and van der Waals or ionic forces). The free volume theory states plasticization as a way to increase free volume (Santosa & Padua, 1999; Suyatma et al., 2005). Glycerol is a major by-product of biodiesel production which has significantly increased, thus creating a significant surplus and is often regarded as a waste stream with an associated cost (Fountoulakis & Manios, 2009; Gu & Jérôme, 2010). The use of glycerol as plasticizer in these films can be a way to help solving the existing surplus of this co-product from biodiesel production. Lipids, due their hydrophobic behavior, are added to polysaccharide films aiming at decreasing their hydrophilicity, consequently decreasing their water affinity (Vargas, Albors, Chiralt, & González-Martínez, 2009). From all the commercial oils, corn oil has shown to be one of the most effective, in comparison with others, in decreasing the water vapor permeability of polysaccharide and protein films (Ekthamasut & Akesowan, 2001; Tanaka, Ishizaki, Suzuki, & Takai, 2001).

The aim of this study was to evaluate the influence of glycerol and corn oil presence in the properties of the films. This was achieved by relating the information gathered from Fourier-transform infrared spectroscopy, thermal analyses (DSC and TGA), solubility measurements, moisture content determinations, water vapor permeability measurements and mechanical tests.

2. Materials and methods

2.1. Films preparation

Chitosan film-forming solutions were prepared dissolving chitosan (deacetylation degree of 90% approximately, Aqua Premier Co., Thailand) (1.5% w/v) in a lactic acid (1.0% v/v) solution (Merck, Germany) with agitation using a magnetic stirrer (at 200 rpm) overnight at room temperature (20 °C); Tween 80 (0.2%) (Acros Organics, Belgium) was also added as surfactant. Galactomannan film-forming solutions were prepared by dissolving *G. triacanthos* galactomannan (obtained as described in Cerqueira, Pinheiro, et al. (2009)) (1.5% w/v) in distilled water, followed by the same conditions as for chitosan. Glycerol (87%, Panreac, Spain) was added at three different concentrations (0.5, 1.25 and 2.0% w/v). Corn oil (Sovena, Portugal) was added at three different concentrations (0.25, 0.5 and 0.75% w/v) under agitation during 20 min at 60 °C, to films with constant concentrations of 1.5% of polysaccharide and 0.5% of glycerol. To produce the films, a constant amount (13 mL) of film-forming solution was cast onto a 5.7 cm diameter Petri plate. The films were dried in an oven at 35 °C during 16 h. Films were maintained at 23 °C and 54% RH at least 24 h before performing the tests (these conditions were obtained in a desiccator through a saturated salt solution of Mg(NO₃)₂).

2.2. Moisture content

To determine the moisture content of films about 50 mg of film were dried at 105 °C during 24 h (until the equilibrium weight was attained). The weight loss of the sample was determined, from which the moisture content was calculated using the following equation:

$$\text{Moisture content} = \frac{(M_i - M_f)}{M_i} \times 100 \quad (1)$$

where M_i and M_f are the masses of initial and dried samples, respectively.

2.3. Fourier-transform infrared (FTIR) spectroscopy

The IR spectra of the films were determined using an infrared spectrometer (FTIR) (Perkin–Elmer 16 PC spectrometer, Boston, USA), in Attenuated Total Reflectance mode (ATR) between 400 and 4000 cm⁻¹, using 16 scans at a resolution of 4 cm⁻¹. Before film analysis, an open bean background spectrum of clean crystal was recorded. Data analysis of each film was performed with Peak Fit 4.12 (SYSTAT Software Inc., Richmond, CA, USA) program. Spectra of films have been deconvoluted with the second derivative method with a smoothing filter set at 15%.

2.4. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

Differential scanning calorimetry (DSC) measurements were performed with a Shimadzu DSC-50 (Shimadzu Corporation, Kyoto, Japan) calibrated with Indium as standard. Ca. 10 mg of the sample was placed in aluminum DSC pans (Al crimp Pan C.201-52943). The measurements were performed between –100 and 250 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. In a first heating scan the enthalpy of melting (ΔH_m) and the melting peak (T_m) were determined; a second heating allowed the measurement of glass transition temperature (T_g). Thermogravimetric analysis (TGA) was completed with a Shimadzu TGA-50 (Shimadzu Corporation,

Download English Version:

<https://daneshyari.com/en/article/604385>

Download Persian Version:

<https://daneshyari.com/article/604385>

[Daneshyari.com](https://daneshyari.com)