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Influence of plasticizers in pectin films: Microstructural changes

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HIGHLIGHTS

- Pectin microstructural changes were evidenced using plasticizers.
- GLY plasticizer increased the predominant amorphous character of pectin.
- GLY acts as an internal plasticizer.
- PEG was a separate phase in the pectin matrix.
- PEG acts as an external plasticizer.

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ABSTRACT

This study investigated the effect of two plasticizers, i.e. glycerol (GLY) and polyethylene glycol (PEG), on pectin film structure. The results reveal that glycerol acts as an internal plasticizer. GLY increased the predominant amorphous character of the plasticized films because of decreased intermolecular attraction, resulting in low temperature degradation and allowing the conformational transformation of the galacturonan ring via a boat conformation. Glycerol produced more deformable and weaker films. Also, glycerol led to films with a greater Swelling Index (SI) and Water Vapor Permeability (WVP) value. When PEG was used as the plasticizer, films were also weaker and a lower Young's modulus was obtained compared to the neat pectin film. However, with increasing PEG MW, more compacted films were obtained, resulting in less deformable films. The WAXD spectra and DSC thermograms indicate that PEG existed as a separate phase in the pectin matrix. Moreover, the pectin phase became more compacted and less permeable to water vapor as the PEG MW is increased. These results show that PEG acts as an external plasticizer.

1. Introduction

Pectin is one of the naturally occurring polysaccharides that has become more and more important over recent years, because this is a material with ecofriendly properties primarily due to the renewability and sustainability of their sources, renewable. The pectin has low cost, because of their abundance in nature. The potential applications of pectin are numerous and involve different fields such as fibers for the textile industry, medical products, cosmetics, bioimplant, delivery of drugs, herbicides, fungicides [1–3]. Pectin is a structural component of the vegetal cell wall, typically isolated from plants of economic importance (citrus, sugar beet, apple, etc.). It is composed of an anionic complex polysaccharide based on chains of linear regions of (1 → 4)-α-D-galacturonosyl units and their methyl esters, interrupted in places by (1 → 2)-α-L-rhamnopyranosyl units. Fractions of these rhamnopyranosyl residues are branch points for neutral sugar side chains of (1 → 5)-α-L-arabinofuranosyl or (1 → 4)-β-D-galactopyranosyl residues [4,5]. Pectin has a strong hydrophilic character and needs to be cross-linked to prevent dissolution. Its functional groups (-OH, -COOH, $-COOCH_3$) enable it to interact with several compounds such as glutaraldehyde (GTA), divalent ions (Ca^{2+}, Mg^{2+}), and diimines, among others [6]. GTA is a common cross-linking agent frequently used in biopolymers because of its excellent reactivity and low cost. However, it has shown some cytotoxicity [7] which can be diminished by washing with ethanol-water solutions. Cross-linking involves the reaction between hydroxyl groups of pectin and aldehyde groups of GTA [8], and the concentration of the cross-linking agent can be used to modulate biopolymer properties [9]. Cross-linked pectin results in a more

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brittle character, which often requires the use of a plasticizer in order to make a sufficiently flexible film. The addition of a suitable plasticizer produces micro-structural changes in the polymer matrix, involving a reduction in the intermolecular forces between polymer chains [10]. Simultaneously plasticized films show an unfavorable increase in gas and vapor permeability and a loss of mechanical properties. Moreover, above a critical concentration of the plasticizer, phase separation or at least plasticizer exclusion from the polymer matrix can occur. Commonly used plasticizers in biopolymers are sorbitol, polyols, and glycerol [10,11]. Also, Polyethylene glycol (PEG) is a biocompatible, nontoxic polymer with good water solubility. It is an efficient plasticizer for bio-polymers, nanocomposity and is a frequently additive used in pharmaceutical preparations [12].

In this study, we evaluated the effect of two plasticizers, i.e. glycerol (GLY) and polyethylene glycol (PEG), in the structure of pectin films. Several concentrations of GLY and different molecular weights of PEG were used. Micro-structural changes were assessed by wide angle X-ray diffraction (WAXD). The barrier and mechanical properties were also determined in order to evaluate the performance of prepared films.

2. Experimental

2.1. Materials

Pectin from Citrus Fruits (CAS 9000-69- degree of methyl esterification, 6.7%, MW = 30–100 kg mol^{-1}) was purchased from Sigma–Aldrich (Denmark). Glutaraldehyde commercialized as 25% Grade II was purchased from Sigma–Aldrich (St. Louis, MO, USA). glycerol, acetone, N,N-dimethylformamide, NaOH, HCl and ethanol were provided by BioPack (Campana, Argentina). PEGs from 200 to 1000 g/mol were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Film preparations

Neat and plasticized films were obtained from aqueous solutions containing 2% w/v of pectin at 40 °C. Plastified films were obtained adding different amounts of GLY to the pectin solution in order to obtain concentrations ranging from 0 to 5% w/v or PEG of different molecular weights (from 200 to 1000 Da) at a concentration of 1% w/v. Film forming solutions were cast in Petri dishes (14.5 cm internal diameter) and dried in an oven at 60 °C for 24 h. After that, the films were cross-linked with 50 mL of acetone containing 5% (w/v) glutaraldehyde (Sigma Aldrich) and 1% (w/v) HCl. Finally, the films were washed with ethanol and water. Film preparation was carried out in triplicate. Dried films had similar thickness (approximately 250 μm thick).

2.3. Solubility assays

Samples were dried at 40 °C in an oven-dryer for 24 h and then the initial solids content was measured by weighting. Samples were put in a 50 mL beaker with 30 mL solvent and sealed by Parafilm, and then placed in a thermostat at 25 °C for 48 h. Films were dried for 24 h in a dry oven and then the solid contents were measured. Solubility (%) of film was defined as ratio of the water soluble solids to the initial solids content. Solubility assays were carried out by treating the films with several solvents: acetone (Ac), ethanol (Eth), N,N-dimethylformamide (DMF), and water at 25 °C.

2.4. FTIR analysis

The FTIR spectra were determined by mode using Nicolet PROTEGE 460 Spectrometer over the range 400 e 4000 cm^{-1}. The number of scans for each sample was 64.

2.5. UV-VIS spectroscopy

UV-VIS spectra of acetone and aqueous extracts of fresh prepared films were recorded on UV-VIS U-2001 Hitachi spectrophotometer over the wavelength range 200–1000 nm.

2.6. Wide angle X-ray diffraction (WAXD)

The X-ray diffraction analyses were carried out in a range of 2θ between 0° and 60° using a Rigaku model D-Max III C device (Tokyo, Japan), a CuKα lamp and a nickel filter. From the diffractograms, the d-spacing (d_{sp}) of each synthesized film was determined by Bragg's equation (Eq. (1)).

$$n\lambda = 2d\,sin\theta \quad (1)$$

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar distance or intersegmental distance, and θ is the angle between the incident rays and the plane of scattering. All analyzed samples were conditioned in a humidity- and temperature-controlled chamber for 24 h at 25 °C and 40% relative humidity (R.H.). Diffractograms were fitted using ORIGIN PRO 8 software and the first derivate was used to identify the curve maximum.

2.7. Differential scanning calorimetry (DSC)

The DSC curves were obtained at 10 K/min under a nitrogen atmosphere (Mettler Toledo DSC 831, Giessen Germany). Two scans were performed with each sample, the first from −50 °C to 80 °C in order to remove the thermal history of the samples, and the second from −50 °C to 500 °C.

2.8. Mechanical properties

Tensile tests of the synthesized films were performed at room temperature using a Comten Industries (Series 94 VC) device (Pinellas Park, Tampa FL, USA). Films were cut into strips with a width of 1.1 cm and length of 4.0 cm. To ensure complete relaxation of the polymeric structures and to standardize the experimental procedure, film samples were stored in a humidity- and temperature-controlled chamber for 24 h at 25 °C and 40% R.H. The polymeric strips were then fixed between upper and lower clamps of the tensile tester and the tensile strength was determined at a constant traction speed of 5 mm/min. The mechanical parameter data include the average values from three samples of each film. The film thickness was measured using a Köfer micrometer (precision ± 1 μm) (Germany).

2.9. Swelling index (SI)

An area of 1 cm^2 of each film was vacuum dried in an oven at 50 °C for 24 h. The dried film was accurately weighed (W_d) and immersed in a flask containing 50 mL of distilled water at 25 °C. After 12 h, swollen samples were withdrawn from the aqueous medium, surface dried to removal of excess surface water by light blotting with tissue paper and weighed (W_w). All experimental trials were carried out in triplicate. The swelling index was determined by the following equation:

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