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Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach

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Abstract

The effects of glycerol and sorbitol on the water sorption isotherms and water vapor permeability (K^w) of cassava starch films prepared by casting were investigated. K^w values were determined in three ranges of relative humidity, RH, (2–33%, 33–64% and 64–90%) and the GAB model was used to fit experimental water sorption isotherms. These data were used to determine the relative influence of the diffusion coefficient of water (D^w) and the average solubility coefficient ($\bar{\beta}$) of water in the films on the K^w value. In all cases, an increase in K^w values were observed with increasing plasticizer concentration and RH. The D^w, $\bar{\beta}$ and K^w values of films prepared with glycerol were greater than those of films prepared with sorbitol. For high RH, the $\bar{\beta}$ values increased 6-fold for films with glycerol and 7-fold for films with sorbitol, while D^w values did not change significantly. These results indicate that K^w values are dependent on the solubility coefficient ($\bar{\beta}$) of water in the film, which is not consistent with the proposal that an opening of polymer chains promoted by plasticizers leads to an increase in D^w and K^w.

Keywords: Starch films; Water permeability; Solubility approach

1. Introduction

The increase in non-biodegradable waste material and the difficulty in recycling most of the available synthetic packaging have been pushing researches toward the development of new biodegradable materials, which are suitable for packaging. In this regard, the production of edible films may play an important role in food preservation (Krochta & Miller, 1997; Lu, Weng, & Cao, 2006; Monterrey & Sobral, 1999; Myllärinen, Partenen, Seppälä, & Forssell, 2002).

The obtainment of films based on biological materials involves the use of at least a film-forming agent (macromolecules like starch or proteins), a solvent and a plasticizer (e.g., glycerol and sorbitol) (Krochta, Baldwin, & Nispero-Carriedo, 1994). Several studies have been carried out on the use of starches from different sources to obtain films and coatings with different properties. The reported results indicate that these carbohydrates are promising materials in this regard (Garcia, Martinho, & Zaritzky, 2000; Defloor, Dehing, & Delcour, 1998; Souza & Andrade, 2002; Avérous, Fringant, & Moro, 2001; Mali, 2002; Nogueira, Mazoni, Mali, & Grossmann, 2003; Myllärinen et al., 2002; Larotonda, Matsui, Sobral, & Laurindo, 2005).

Film characteristics are dependent on the cohesion of the polymeric matrix, which in turn is dependent on the structure of the polymer chains, the film obtainment process and the presence of plasticizer agents. The most used plasticizers for starch-based films are sorbitol and glycerol (Gontard & Guilbert, 1996; McHugh & Krochta, 1994; Krochta & Miller, 1997; Lourdin, Coignard, Bizot, & Colonna, 1997).

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The incorporation of plasticizers is necessary to reduce polymer intermolecular forces, increasing the mobility of the polymeric chains, and improving the mechanical characteristics of the film, such as the film extensibility (Krochta & Sothornvit, 2001; Mali, 2002). Also, plasticizers affect the water barrier property of the films, since they have a great affinity for water.

Godbillot, Dole, Joly, Rogé, and Mathlouthi (2006) reported that water content and interactions in starch films are dependent not only on plasticizer concentration, but also on the relative humidity (RH) to which these materials are exposed. They reported that the interactions between the components of the system, formed by starch, plasticizer and water, vary according to the relative quantities of these components. It is possible that, under some conditions, phase separation occurs.

Reports found in the literature describe the behavior of water vapor permeability and the simultaneous behaviors of water diffusivity and solubility in a polymeric matrix (Krochta & Miller, 1997; Krochta & Sothornvit, 2001; Larotonda et al., 2005; Martelli, Moore, Paes, Gandolfo, & Laurindo, 2006a; Martelli, Moore & Laurindo, in press; Moore, Martelli, Gandolfo, Sobral, & Laurindo, 2006). However, no specific studies were found in the literature regarding the relative influences of these parameters on the water vapor permeability of starch films.

Larotonda et al. (2005), working with Kraft paper impregnated with starch acetate, investigated the influence of the impregnation on the values for the water vapor permeability (K^w), water diffusion coefficient (D^w) and the solubility coefficient of water in this material. Through the first derivative of the water sorption isotherm of Kraft paper (represented by the GAB model) in relation to the water activity (a_w), divided by the water vapor pressure at the sorption isotherm temperature, the value of the solubility coefficient (β) of water in the film was calculated and called film hydrophilicity by these authors. From the behavior of the average β value (averaged over a relative air humidity range and represented by $\bar{\beta}$) in relation to the water activity of the films, the water diffusion coefficients (D^w) were determined, since K^w is dependent on the product of these variables. This procedure is summarized by Eqs. (1)–(3)

$$K^w = \rho^s \cdot D^w \cdot \bar{\beta} \tag{1}$$

where the K^w unit is g m/m^2 h Pa, ρ_s is the film density (g/m^3), D^w is given in m^2/h and $\bar{\beta}$ is given in g of water/g of dry solid × Pa.

$$X_w = \frac{C k m_o a_w}{[(1 - k a_w)(1 - k a_w + C k a_w)]} \tag{2}$$

$$\beta = \frac{C k m_o}{p_s}\left[\begin{array}{l}\frac{1}{(1-ka_w)(1-ka_w+Cka_w)} - \\ \frac{a_w}{[(1-ka_w)(1-ka_w+Cka_w)]^2}[-k(1-ka_w+Cka_w) \\ +(1-ka_w)(-k+Ck)]\end{array}\right] \tag{3}$$

In Eqs. (2) and (3), a_w is the water activity (RH/100), X_w the equilibrium water content on a dry weight basis, m_o the water content on a dry weight basis related to the monomolecular water layer, C the Guggenheim constant relating to the monolayer heat sorption, and k the constant relating to the multilayer heat sorption. The saturation pressure of water, at the temperature at which the sorption curve was obtained, is represented by p_s.

Moore et al. (2006) reported data on the influence of $\bar{\beta}$ and D^w on the water vapor permeability of keratin-based films plasticized with glycerol. These authors report that the value of K^w increased about 6-fold when 0.09 g glycerol/g of keratin was added to the film-forming solution. This large increase in K^w was explained by the increase in the solubility coefficient ($\bar{\beta}$) of the water in the films. For relative air humidity (film water activity) values ranging from 0.62 to 0.96, $\bar{\beta}$ varied from 3.18×10^{-6} to 5.43×10^{-5} g water/g dry mass Pa (17-fold increase), while the value of the diffusion coefficient D^w decreased from 5.83×10^{-6} to 1.26×10^{-6} m^2/s. Small variations in the thickness and density of the films also influenced the K^w values of the films, but the overall results indicated that K^w values of keratin films are dependent on the $\bar{\beta}$ values.

The objective of this study was to investigate the effects of glycerol and sorbitol concentrations and of the relative air humidity on the water vapor permeability, water diffusion coefficient and the solubility coefficient of water in cassava starch films.

2. Materials and methods

2.1. Film preparation and characterization

Starch films were prepared through the casting technique using a film-forming solution containing 3% of commercial cassava starch (Yoki, Brazil). Glycerol and sorbitol were used as plasticizers, at concentrations of 0.25, 0.30 and 0.35 g/g dry starch. The mixture was heated to 80 °C in a thermal bath under constant stirring, and poured homogenously onto Plexiglas plates. The plates with the film forming solution were then dried in an oven with air circulation, at 40 °C, for 16 h. The dry films were removed from the plates and conditioned for 48 h in glass desiccators at a relative humidity of 58% (using a saturated solution of sodium bromide) and temperature of 25 °C.

2.2. Film thickness and density

The film thicknesses were determined using a digital micrometer (Mitutoyo Co., Japan) from the average of ten random measurements performed for each film. Square samples of the films (20 × 20 mm) were kept in desiccators with phosphorus pentoxide (P_2O_5) for 20 days, at 25 °C, and then weighed. The thicknesses of these films were measured at five different points of each sample. The film den-