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Microstructure and color of starch–gum films: Effect of gum deacetylation and additives. Part 2

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Abstract

Xanthan gum deacetylation, additives (sucrose, soybean oil, sodium phosphate and propylene glycol) and pH modifications influence on cassava starch-based films microstructure and color has been studied. X-ray diffraction and microscopic analysis have demonstrated that sucrose addition influenced ($p < 0.05$) the film crystallinity during 60 days storage (75% RH, 23 °C). Although not enough to prevent sucrose crystallization, deacetylated xanthan gum addition delayed the crystallization process. Comparing to the control, only cassava starch concentration and the additives sucrose and sodium phosphate affected samples total color difference (ΔE). However, all samples presented high lightness and low color values for '*a*' redness and '*b*' yellowness, indicating that, independent of the additives or pH modifications, the materials were almost colorless, with a high brilliancy.

Keywords: Biofilms; Microstructure; Color; Starch; Xanthan gum

1. Introduction

Although there are low cost, renewability and biodegradability (Avérous, Fringant, & Moro, 2001) advantages of using starch-based films, they present low mechanical resistance and high moisture sensitivity when compared to traditional petroleum plastic films (Martin, Schwach, Avérous, & Couturier, 2001).

Veiga-Santos, Oliveira, Cereda, Alves and Scamparini (2005) have observed that cassava starch-based films, with no additives, presented higher tensile strength resistance (59.41%), and lower elongation at break (−4833.08%) when compared to PVC films, indicating that elongation at break is the most disadvantageous mechanical characteristics of the cassava starch-based films and efforts should be made to increase such property.

It was also observed that sucrose, which had demonstrated a higher plasticizing efficacy when comparing to sorbitol and glycerol (Arvanitoyannis, Psomiadou, & Nakayama, 1996), increased cassava starch-based films elongation at break (from 3.99 to 120.62%) (Veiga-Santos et al., 2005). Sucrose addition to biodegradable films was also investigated by Cuq, Gontard, Cuq and Guilbert (1996) and Sothornvit and Krochta (2000). Although neither study have investigated crystallinity parameters, Sothornvit and Krochta (2000) have reported crystallization after one month storage, indicating that sucrose can affect the material structure during storage.

Deacetylated xanthan gum addition resulted in higher elongation at break when compared to the same films with the acetylated xanthan gum added (Veiga-Santos et al., 2005). However, removing the acetyl groups from xanthan gum inner mannose allows the polymer chain to associate with the other film components (Morris, Gontard, Hember, Manning, & Robinson, 1996), which could, therefore, affect material structure. Although Chen and Nusinovitch (2000, 2001) have already introduced xanthan gum into wax-based coatings, the effect of xanthan gum addition, deacetylated or not, on starch films structure, have not yet been investigated.

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Propylene glycol reduces cassava starch-based films tensile strength (Veiga-Santos et al., 2005) probably due to its plasticizer character (Lacroix, Jobin, Mezgheni, Srour, & Boileau, 1998). However, its addition in low concentrations may prevent possible sucrose crystallization due to its humectant's character, justifying the attempt in investigating its effect on starch–gum films microstructure.

Moisture sensitivity of hydrophilic films may be reduced by addition of hydrophobic materials (Garcia, Martino, & Zaritzki, 2000; Yang & Paulson, 2000). However, when waxes and long chain saturated fatty acids and fatty alcohols are utilized, a reduction on the optic properties of the films may be observed (Yang & Paulson, 2000). In attempt to avoid or reduced optical interferences due to lipids addition, the use of unsaturated lipid additives such as soybean oil would be recommended. Soybean oil utilization as additives has already being reported (Garcia et al., 2000; Yang & Paulson, 2000), although the homogeneity patterns of starch–soybean oil films have not been extensively investigated.

Orthophosphate group with acidic function, such as monosodium phosphate, forms an ester linkage with one of the hydroxyls in the starch chain, producing starch phosphate monoesters. The introduction of such ionizing groups may cause a small separation between the molecules (Ellinger, 1972), which may alter the microstructure of starch films added with sodium phosphate.

In previous study of this series, important elongation at break increase were observed studying the influence of xanthan gum (deacetylated or not), additives (sucrose, propylene glycol, soybean oil and sodium phosphate) and pH modifications on cassava starch–xanthan gum films. In order to evaluate the feasibility of using the selected additives, films produced by the same experimental design studied previously (Veiga-Santos et al., 2005) was evaluated for microstructure and color. For that matter, crystallinity, microscopy and color parameters were investigated.

2. Material and methods

2.1. Materials

Commercial cassava starch (Flor de Lotus, Brazil), acetylated xanthan gum-rodigel (Rhodia, Brazil), deacetylated xanthan gum (CP Kelco SA, Brazil) and soybean oil (Cargill Agricola SA, Brazil), and analytically pure sucrose, propylene glycol and monobasic sodium phosphate (Synth, Brazil).

2.2. Sample preparation

Cassava starch (3–5 g/100 g film forming suspension) was blended with water and the additives: acetylated or deacetylated xanthan gum (0–1 g/100 g film forming suspension), sucrose (0–2 g/100 g film forming suspension), propylene glycol (0–1 g/100 g film forming suspension), sodium phosphate (0–0.2 g/100 g film forming suspension) and soybean oil (0–0.06 g/100 g film forming suspension), considering the total weight of the film forming suspension. The pH was adjusted (4–8) with 50% citric acid solution or 5% sodium hydroxide solution, heated to 75 °C with constant stirring and placed under vacuum (30 min), to remove bubbles that could become pinholes after film drying. The films were prepared according to the casting technique, by dehydrating 30 g of the film forming suspension over a Petri plastic dishes, under renewable circulated air (30° ± 2 °C). Films containing 5 g cassava starch/100 g film forming suspension with no additives or pH adjustment were considered as the control. Samples were storage (23 °C, 75% RH) for at least 4 days prior to testing. In order to investigate microstructure since the first day of storage, crystallinity analysis of no-conditioned samples at 1 day storage were also performed.

Since starch-based films have a hydrophilic character (Avérous, Moro, Dole, & Fringant, 2000), 75% relative humidity was chosen to conditioning the experimental films in order to evaluate the material performance on high content moisture environment. Although 50% RH is more often utilized (Avérous et al., 2001; Gontard, Guilbert, & Cuq, 1992) for preconditioning biodegradable films, 75% RH is also utilized (Ruotsalainen, Heinämäki, Guo, Laitinen, & Yliruusi, 2003; Trezza & Krochta, 2000).

2.3. Microstructure analyses

2.3.1. Crystallinity

The relative crystallinity of the films was investigated by wide-angle X-ray diffraction (WAXS). Measurements were carried out using a DMAX-2200 Rigaku International Corporation $\theta/2\theta$ diffractometer, operating with voltage of 40 kV and amperage of 20 mA, with Cu Kα radiation. Samples were fixed at an aluminum sample holder, and analyzed from 5 to 60° (2θ), with angular step of 0.1° (2θ), and sampling interval time of 3 s. The films were analyzed at each 15 days, during a storage period of 60 days (75% RH, 23 °C), in duplicate. Crystallinity was also investigated (at same conditions) for the native cassava starch and sucrose in order to obtain crystallinity standards.

2.3.2. Light microscopy

Samples surface was observed with LEICA-DMLP by transmitted light microscope, with no further preparation. Images 200×-magnification was collected with a CCD camera.

2.3.3. Scanning electron microscopy (SEM)

SEM digital images of the samples surfaces and fractures were obtained by a Jeol JSM-5900LV scanning electron microscope. Cross-section images were obtained by cryogenic fracture of the films using liquid nitrogen. Samples