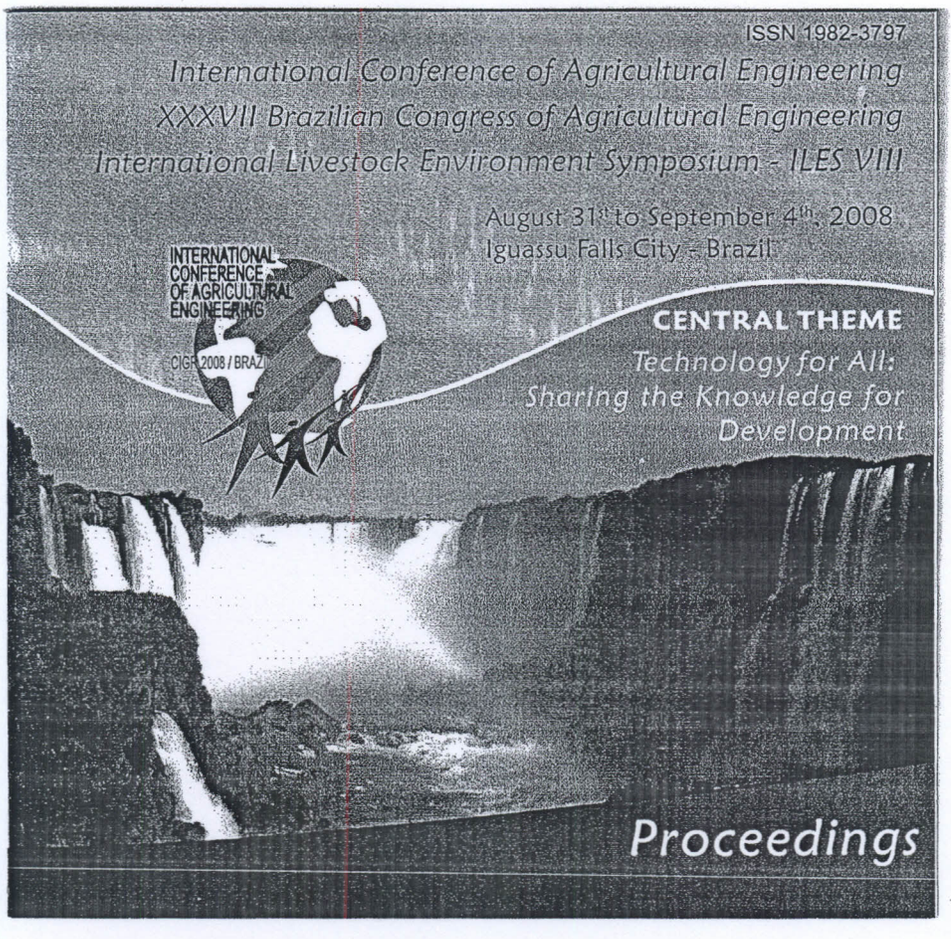

INTERNATIONAL CONFERENCE OF AGRICULTURAL ENGINEERING
CIGR 2008 / BRAZIL
ISSN 1982-3797
August 31st to September 4th, 2008
Iguassu Falls City - Brazil
Conference of Agricultural Engineering
an Congress of Agricultural Engineering
tock Environment Symposium - ILES VIII
Proceedings


ISSN 1982-3797
International Conference of Agricultural Engineering
XXXVII Brazilian Congress of Agricultural Engineering
International Livestock Environment Symposium - ILES VIII
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CENTRAL THEME
Technology for All:
Sharing the Knowledge for Development
Proceedings

CIGR - International Conference of Agricultural Engineering
XXXVII Congresso Brasileiro de Engenharia Agrícola

Brazil, August 31 to September 4, 2008

A COMPARISON OF CHITOSAN AND ZEIN PROTECTIVE EDIBLE COATING ON SLICED APPLES

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Presented at
CIGR INTERNATIONAL CONFERENCE OF AGRICULTURAL ENGINEERING
XXXVII CONGRESSO BRASILEIRO DE ENGENHARIA AGRÍCOLA – CONBEA 2008
Brazil, August 31 to September 4, 2008

ABSTRACT: Protective treatment of minimally processed and post harvest products entails a variety of different techniques, including controlled cold room environment, ozone washing, biocidal action by irradiation and protective measures throughout packaging and coatings. Recent emerging technology provides the ability to apply biobased edible materials on freshly cut surfaces, offering an alternative method of controlling and extending the quality and shelf life during storage. In this paper we compare the polysaccharide chitosan and the maize protein zein as potential material for edible coatings on cut apples, concerning protective features as mass loss and visual. The sensory properties evaluated by means of visual aspect maintenance (colorimetry). The first is a hydrophilic polymer and the second a high hydrophobic protein. The gel preparation and surface deposition methods are described within.
KEYWORDS: edible film, chitosan, zein, minimally processed, natural polymers.

INTRODUCTION: Fruits and vegetables are some of the fastest-growing sales within the food market, experiencing exponential sales growth in the past decade. In particular, the consumption of fresh-cut fruits is increasing tremendously, reflecting a general consumer's tendency to purchase most of them as "ready-to-eat" (often sliced) sorts at street retail shops and market places. The worldwide market for the "minimally processed" fruits is expected to continuously increase by nearly 30% per year (CARDWELL, 2005).

Fresh-cut fruits, however, present many technical problems since the damaged tissues spoil faster than sound ones. Also during peeling, cutting and shredding, the fruit's surface is exposed to air and consequently to contamination by microorganisms. In most cases, processed products are more perishable than the unprocessed intact raw products from which they originate.

It is not only their nutritional property, but also the physical appearance, aroma and flavor that strongly influences the sales of minimally processed products. As pointed by NASSU et al., 2001, the consumer's primary concern in buying processed products is that of a fresh-like appearance with a texture reasonably absent of defects. The maintenance of such features is quite a challenge.

Protective treatment of minimally processed products entails a variety of different techniques, being the use of edible coatings, probably the cheaper and easier method as compared to other preservation methodologies. Edible coatings can create a modified atmosphere similar to controlled atmosphere by modifying internal gas composition retarding ripening and reducing decay.

The polysaccharide chitosan and the natural protein zein have been proposed as a potential material for edible coating usage with satisfactory preservative properties (BAI et al., 2003; ASSIS & PESSOA, 2004). Chitosan is a natural linear hydrophilic polymer, formed primarily of repeating units of beta (1-4) 2-amino-2-deoxy-D-glucose (or D-glucosamine) which a structure similar to cellulose.

The antibacterial and antifungal effects of chitosan have been evaluated by NO et al., 2002. On the other hand, zein is the main storage protein in the corn endosperm and makes up more than half the total mass of the seed proteins. Actually, zein comprises a mixture of proteins classified according to

their solubility and molecular rates, being the α-zeins the most abundant, with 75 to 85% of the total maize proteins. The zein proteins display significant hydrophobic properties with ability to form films, suitable for applications as gas and moisture-barrier (BAI et al., 2003) and have effective action on decreasing bacterial population when used as edible coating (CARLIN, et al., 2001). The present work aims to establishment of a basic procedure for preparing film forming chitosan and zein gelatin and compare the protective features concerning surface water sorption, color alteration and loss of mass on coated faces of sliced apples.

METHODOLOGY:

The starting chitosan was purchased from Polymar (Brazil) and used as received. Coating solution was prepared by dispersing the polymer in a 100 mL of distillated water whilst stirring on a magnetic stirrer at room temperature. Acetic acid (0.5 M) was added to initially adjust the solution pH to approximately 4.0. Solution with chitosan concentrations of 10.0 g/L were prepared and allowed to homogenize, under moderate stirring, until complete dissolution. After homogenization the pH of each solution was measured. No plasticizer was added to chitosan formulation.The 10 g/L formulation was adopted in function of the most satisfactory results (homogeneity, stability) previously attained (Assis & Pessoa, 2004; ScramiM et al., 2006)

Zeins were extracted from maize grains which were ground and treated with hexane in soxlhet apparatus (along 24 h) to remove the oil fraction. The residual mass was kept in 0.5 mol/L NaCl aqueous solution for 6 hours to remove the albumins and globulins. The residual mass was mixed with 70% ethanol aqueous solution during 24 h. The zein was obtained by solvent evaporation and then lyophilized (FORATO et al. 2003). Zeins solutions were prepared using 70% ethanol as solvent in a concentration of 10.0 g/L. After solvent evaporation the resultant films are brittle with low tensile strength (SCRAMIM et al., 2006) then propylene glycol (PG) was added as plasticizer in the proportion of 5.0%.

Supermarket apples (cv. Gala) were first sliced into two halves and then individually dipped into the gels. Excess gel was allowed to drain off and the film formed by drying at room temperature. Ten samples were prepared for each formulation and six reference samples were kept without coating.

The apples slices (coated and uncoated) were stored in non-controlled conditions (an ambient temperature of between 25-30 °C and RH of 76%) whilst loss of mass was recorded daily. Weight values were estimated as the average of loss individual weights and the antifungal effect qualitatively assessed by visual rating and colorimetry recording. The brownish of cut surface was measured (Chroma Meter CR-400, Konica Minolta) and expressed as Hunter color values. Chroma (color saturation), total color difference (TCD) and hue angle were calculated from Hunter L, a, b values.

RESULTS AND DISCUSSION:

When deposited on fruit cut surfaces, chitosan forms a high transparent film while zein tends to a yellowish appearance. The surface color evolutions along cut apples surface are summarized in Table 1. It was observed a reduction of 'L' value for chitosan and an increase for zein coated samples when compared to control, what is an evidenced of a reduction on the surface browning due to chitosan coating. It is worth noticing the change observed in the stimulus 'a' (red-green axis).

Table 1. Average change in color on the cut apple surface coated with chitosan and zein solution after two days of storage.

Sample	L	a	b	Chroma	Hue A(°)	TCD
Control	70±2	-0.2±0.8	24.0±0.8	24.0±0.8	-0.6±2	
Chitosan coating	53±3	6±1	24±1	25±1	15±3	18±3
Zein coating	75±4	3±1	37±2	37±2	4±4	14±2

By comparing the control, the values of 'a' changes to more positive figures, indicating a shift towards red color. Similarly, the Hue Angle changed from 0° (yellow) to 90° (red). Stimuli 'b' (yellow-blue axis) and Chroma did not show significant alteration. These observations clearly indicated that the brownish effect was more intense for zein coated samples than for chitosan coated ones.
Concerning protection action, in Figure 1 is presented the relative mass loss against storage time, in non-controlled environment. Data are plotted in comparison to uncoated samples. The transpiration rates are quite similar for the sliced apples along the first 5 days. After that, the best results were attained to zein, showing a minor loss of weight especially over the total period of storage. The hydrophobic nature of zein coating showed to be efficient in reducing transpiration.
WORRELL at al., 2002, has showed that one of the main features of a protective coating is the lower rate of weight loss, i.e., a good film should be able to establish a good difference in vapor pressure between the fruit and its surroundings. Despite the fact that chitosan is assumed to be a hydrophilic material, its protective effect is slightly inferior to the hydrophobic coating, which good results can be attributed to the formation of a homogeneous film with less intrinsic porosity at the concentration used here (10 g/L) (ASSSIS & PESSOA, 2004). This results in a reduced water vapor permeation rate (McHUGH et al., 1993). Nevertheless, all mass loss values (coated and uncoated) converge to similar values for storage times inferior of 5 days.

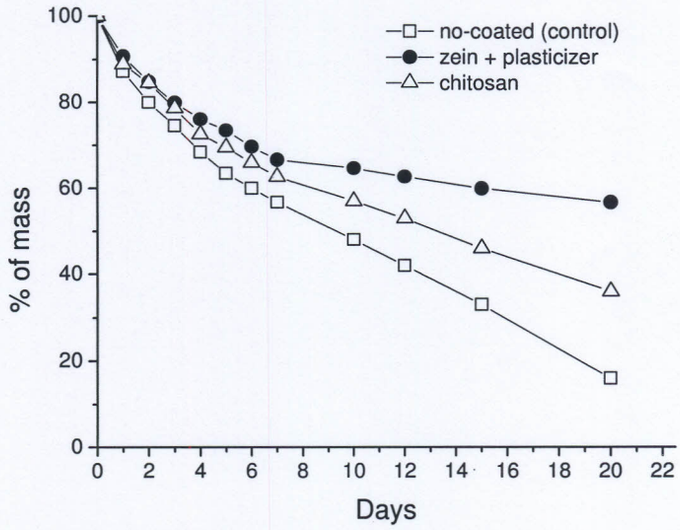

Figure 1. Weight loss in function of storage time (10 g/L film).

Chitosan and zein film formation takes place by means of solvent evaporation. The surface of fresh cut apples is a hydrophilic cuticular layer which presumably facilitates the adhesion of chitosan. High compatibility and adhesion capacity between zein coating were expected to takes place on *in nature* surfaces were the hydrophobic characteristics predominates (CARLIN, et al., 2001).
The characteristics of the cured film are, within certain range, is related to the amount of polymer in precursor gel. Microscopy analysis indicates heterogeneity in the topographic structure as a common feature in all concentrations. After drying, the deposition becomes a tough, flexible porous coating and has thickness less than 1 mm (ASSIS & PESSOA, 2004). Evidently the degree of porosity will have a strong influence on coating permeability. Certain porosity is usually desirable to allow gas exchange, required for aerobic fruit respiration mainly by enabling oxygen and carbon dioxide permeation.

CONCLUSION: Both chitosan and zein are edible, safe for humans and could be used as a protective coating to be applied near harvest time or on cut fruits surfaces. The results showed that chitosan

coating maintains the appearance, reducing browning and surface changes. On the other hand zein has higher protective effect on reducing loss of mass via transpiration.

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