CHITOSAN BIOFILM PROPERTIES AS AFFECTED BY THE ADDITION OF OREGANO ESSENTIAL OIL

UTICAJ ETARSKOG ULJA ORIGANA NA OSOBINE HITOZANSKOG BIOFILMA

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ABSTRACT

In this work, effect of adding essential oil of origano (OEO) into chitosan edible film was studied. Different amount of OEO, from 0.2 to 0.8% v/v was added to the film forming solution containing 0.4% w/v of chitosan. Control sample was produced without oil. Effect of growing oil content on film water sensibility was investigated. Pure chitosan film is hydrophilic and sensitive to water. It swells and partially dissolves in water. Addition of hydrophobic OEO lowered film water sensitivity, regarding film water content and swelling property. Film dissolution in water wasn’t reduced, probably because OEO molecules diffused from chitosan film into water. Color change of chitosan film with addition of OEO was also investigated. Film greenness and lightness decreased until film yellowness and redness increased. Seen by naked eye, films became milky, opaque and whitish to yellowish.

Key words: packaging, properties, biopolymers, chitosan, origano.

REZIME


Proizvod koji se koristi za pakovanje hrane treba biti bezbedan, ekološki prihvatljiv i uočljiv. Hitozan je prihvatljiv, ekološki prihvatljiv i uočljiv proizvod koji se može koristiti za različite aplikacije, među kojima i za pakovanje hrane. Hitozan može biti korisno slanjem u proizvodnju i pakovanju hrane.

Ključne reči: ambalaža, osobine, biopolimeri, hitozan, origano.

INTRODUCTION

Food insufficiency in the world, as a consequence of growing human population brought a demand for greater food production and prolongation of the food shelf life. Food is being transferred to greater distances then ever, all across the Earth. This led to significant development in all the methods of food preservation. Packaging technologies now include packing in five, seven and nine layers high barrier plastic foils, secondary, tertiary and quaternary packaging, with the addition of active components or indicators of the conditions, packing in vacuum, modified atmosphere, in aseptic conditions… (Robertson, 2006). But this over packing became an environmental issue when food processing waste reached 30% of municipal solid waste (Lazić and Novaković, 2010). One of the answers to the problem of packaging waste is composting (Lazić and Novaković, 2010). One of the problems to the answer of the problem of packaging waste (besides reduction, reuse and recycling, incubation with bacteria) is use of biodegradable polymers as a food packaging. They are obtained from renewable resources and biodegrade in environmental conditions in short period of time. Edible biopolymers are a subgroup of biodegradable polymers that can be derived from lipids, proteins and polysaccharides. Often they are produced using material from by products or waste from food industry. Edible packaging makes no waste because it is either consumed with food or can be composted with compostable organic waste and even if it gets in the landfill it degrades quickly after disposal leaving no harmful substances (Lazić and Gvozdenović, 2007, Lazić and Novaković, 2010). One of the polysaccharides that’s being tested for application in food packaging is chitosan. It is produced by deacetylation of polysaccharide chitin. Chitin is constituent of crustacean shells and fungus cell walls. Till now it is being commercially produced from see food production waste and scientists are working on profitable way of producing it from fungus production waste (Chatterjee et al., 2005, Kandasamy, 2005, Shuang, 2004, Wu et al., 2004, Wu et al., 2005). Numerous researchers proved chitosan antimicrobial, antioxidant activity, as well as its biodegradability (Chhabra, 2004, Fimbeau et al. 2006, Jeon et al., 2002, Kandasamy, 2005, Kim and Thomas, 2007, Nicholas, 2003, Ouattaraa et al., 2000, Papineau et al., 1991, Sebiti, et al., 2007, Sudharsan et al., 1992). Chitosan was labeled as GRAS (generally recognized as safe) by FDA (Food and Drug Administration) and since could be used as additive in USA. Besides USA it can be used as additive in many countries (Japan, Norway, Italy, Korea….). It is used in nutrition as a diet fiber, for lowering bad cholesterol level, help for lactose intolerance. In food technology as emulsifier, flavor enhancer, for fruit juice clarification (Kandasamy, 2005, Prashanth, 2007, Shahidi et al., 1999).

Chitosan can be used as a carrier for low molecular weight substances that are slowly relised from the chitosan network.
Many researches are working on active packaging design based on this principle (Ojagh, 2010, Shuang, 2004, Prashanth, 2007, Shahidi et al., 1999). Essential oils from different plants have been used for centuries as food additives, cosmetics and pharmaceuticals (Chinese medicine). Their antimicrobial activity has been well known and proven by many researchers. Recently investigations are going in the direction of implementing plant essential oils as active agents in novel active packaging design that could inhibit growth of foodborne pathogen microorganisms (Delaquis et al., 2002, Elgayyar et al., 2001, Hammer et al., 1999, Ruberto et al., 2002).

MATERIAL AND METHOD

Reagents

Commercial chitosan powder from crab shells, highly viscous was purchased from Sigma-Aldrich Chemical Co. (St. Luis MO, USA). Oregano essential oil (carvacol) was purchased from manufacturer: Aromara, Zagreb, Croatia and glacial acetic acid and Tween20 were obtained from Superlab, Belgrade, Serbia.

Film preparation

Chitosan film forming solutions were prepared by dissolving chitosan powder in 1% v/v acetic acid to reach chitosan concentration of 0.4% w/v. Solution was left stirring overnight on a magnetic stirrer to dissolve chitosan. Different amount of oregano essential oil was then added to the solution. Solution labeled as A0 contained no oil, A1 contained 0.2% v/v, A2 0.4% v/v, A3 0.6% v/v and A4 0.8% v/v of oregano essential oil. Tween 20, as a wetting agent, was added to reach 50% of added amount of oil. Film forming solution was then filtered throw cheese cloth to remove impurities and coated on Petri dish, air dried (25 °C, 0 h). The films were cut into a piece of 1 x 2 cm in size and oven dried sample (20°C, 24 h). Film specimens were placed on the surface of a white standard disk of film (2 cm diameter) were cut, weighed, and immersed in 50 ml of water. After 24 h of immersion at 20°C with occasional agitation, the pieces of film were taken out and dried to constant weight in an oven at 105 °C to determine the weight of dry matter which is not solubilized in water.

RESULTS AND DISCUSSION

Water content

Water content of air dried films is shown in fig. 2. Pure chitosan film was thin and transparent and addition of oregano essential oil led to more thick and opaque films.

Swelling property

The films were cut into a piece of 1 x 2 cm in size and weighted in air-dried conditions (w0). They were then immersed in deionized water (25 °C) for 2 min. Wet samples were wiped with filter paper to remove excess liquid and weighted (w1). The amount of adsorbed water was calculated using equation 2:

\[ \text{Swelling} = \frac{w_2 - w_1}{w_1} \times 100 \]  

where w2 and w1 were the masses of the wet and the air-dried samples (Bigi et al., 2004). The measurement was repeated five times for each type of film, and an average was taken as the result.

Water solubility

The film solubility in water was determined as a content of dry matter solubilized after 24 h immersion in water (Casariego et al., 2008). The initial dry matter content of each film was determined by drying to constant weight in an oven at 105 °C. Two disks of film (2 cm diameter) were cut, weighed, and immersed in 50 ml of water. After 24 h of immersion at 20°C, the initial dry matter content of each film was determined.

Color measurement

Color values of films were measured with Chromo meter (CR-400 Chromo Meter, Minolta Camera Co., Osaka, Japan). Film specimens were placed on the surface of a white standard plate and hunter color parameters (L, a, b) were determined as L (lightness, 0=black, 100=white), a (-a=greenness, +a=redness), and b (-b=blueness, +b=yellowness). Color measurement of film was replicated five times for each film and results were used to find average values for each color parameter.

Statistical analysis

Measurements of each property were made in three or more replicates. Statistical analysis was carried out using Origin version 7.1. Means and standard deviation were calculated. ANOVA test (Bonferoni test), with confidence level of 95% was applied to compare the means of properties.
Fig. 1. Film thickness (mm) (A0-pure chitosan film, A1-film with 0.2%v/v of OEO, A2-film with 0.4%v/v of OEO, A3-film with 0.6%v/v of OEO, A4-film with 0.8% of OEO; Bars represent standard deviation)

Swelling property in water also tells about film water sensitivity. Obtained results are shown in the fig. 3. For the pure chitosan film it wasn’t possible to determine swelling property in water, because it dissolved under testing conditions. For film A1 (0.2%v/v of OEO) it was possible to determine the percent of swelling in water because addition of oil disabled dissolution under testing conditions, and further addition of OEO lowered percent of film swelling in the water. This effect of lowering film swelling in the water is due to OEO hydrophobic nature.

CONCLUSION

Because of its hydrophilic nature chitosan forms films that are sensitive in contact with water. Addition of oregano essential oil lowers water sensitivity of the film. Both air dry film water content and swelling in water can be lowered using described method for film preparation with addition of OEO. As to film solubility, addition of OEO using described method for film preparation didn’t bring expected lowering of film solubility in water. Reason for obtained high values for solubility of films with OEO could be OEO particles diffusion from film into wa-

Another property that can be used to analyze film water sensitivity is film water solubility. As shown in the fig.4 addition of OEO didn’t decrease chitosan film solubility in water, as was expected. One of the possible reasons is that low molecular weight OEO particles diffuse from film into water and this diffusion is registered as dissolution of the film. Optimization of film production process, especially mixing of film forming solution with added OEO could result in lowering water solubility of films.
ter. It is possible that optimization of film preparation process, introducing more intensive mixing in the phase of emulsification could result with wanted lowering of film solubility. Smaller diameter drops of OEO would be better incorporated in chitosan molecule network of the film and effect of OEO diffusion from film into water would be disabled. Addition of OEO to chitosan film changed its color lowering lightness and greenness and promoting redness and yellowness. Films went from being colorless and transparent to milky, opaque and whitish to yellowish. This change is undesirable because it could change color of packed food and doing so affect consumer acceptance of product. It would be useful to optimize described method for film production to minimize water sensitivity of pure chitosan film and bring his commercial application for food packaging one step closer.

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