Influence of Different Concentrations of Glycerol and Guar-xanthan on Properties of Pumpkin Oil Cake-Zein Bi-layer Film

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Summary: The objective of this study was to examine influence of glycerol and guar-xanthan in different concentrations on bilayer film based on pumpkin oil cake (PuOC) and corn zein, and to find optimal concentrations of these additives which result in film with optimal mechanical and barrier characteristics. Different concentrations of glycerol (30%, 40%, and 50%) as plasticizer and guar-xanthan (0.1%, 0.3%, and 0.5%) as a stabilizer were added in PuOC layer, while zein layer stayed unchanged in all film compositions. Obtained results showed that the optimal mechanical properties had film with the lowest concentration of glycerol (30%) and the highest concentration of guar-xanthan (0.5%). Films showed poor barrier for water vapour, typical for biopolymer-based films. However, all tested films were very good barrier to \( \text{O}_2 \) (transmission rate lower than 50 ml/m\(^2\)/day at 1 bar). On the other hand, with increase of concentration of added substances, transmission rate of \( \text{CO}_2 \) increased.

Key words: biopolymers, pumpkin oil cake, additives, bi-layer films, properties

Introduction

The ability to decompose in environment, as well as the fact that they are isolated from natural sources, makes biopolymers one of the most interesting topics for researchers in different fields of their possible applications. Today, biopolymers have wide application in pharmacy, medicine, agro and food industry. In recent years, there has been a great interest in biopolymers obtained from agro-industrial waste. Due to their chemical composition (proteins, polysaccharides and lipids), agro-industrial by-products, present a real potential in the production of environmentally friendly plastic (Lazić & Novaković, 2010; Lazić & Popović, 2015).

Pumpkin oil cake (PuOC) is a by-product, obtained after cold-pressing oil extraction from pumpkin seed. PuOC contains the least-processed form of pumpkin seed protein having approximate composition 63% proteins, 12% carbohydrates, 4.5% crude fibers, 8.4% oils and 13% other components (Peričin et al., 2007). Popović et al. (2011) produced biodegradable films based on PuOC that showed good mechanical and gas barrier characteristics. However, in order to produce biodegradable pouches, these films were ineffective in forming heat seal under different conditions of heat time and pressure (Popović et al., 2015). To enable heat sealing of this promising materials, zein layer was casted as second layer on dried PuOC film (Popović et al., 2015).

Zein is the major storage protein of corn and comprises approximately 45–50% of the protein in corn. Zein can form tough, glossy, hydrophobic, greaseproof coatings that are resistant to microbial attack, with excellent flexibility and compressibility. One of the most promising applications of zein appears to be for biodegradable films and plastics used for packaging (Shukla & Cheryan, 2001; Ghasnbarzadeh & Orromiehi, 2009; Pol et al., 2002).

However, without addition of plasticizers, stabilizers and other additives, obtained biopolymer-based films are, usually, very rigid and not handable.

Plasticizers are small molecular-weight, hydrophilic, non-volatile substances that can be added to bio-based films and improve their flexibility and mechanical properties (Embuscado & Huber, 2009; Skurtys et al., 2010). Plasticizers affect intermolecular interactions between polymer chains by reducing the strength of intermolecular forces and, in this way, increase elasticity.
Common plasticizers used in edible films and coatings are typically polyols, including glycerol, propylene glycol, polypropylene glycol, sorbitol and sucrose, with water being the most efficient plasticizer. Fatty acids have also been used as plasticizers in edible films and coatings, though they are not as common (Embuscado & Huber, 2009). Glycerol is plasticizer with the widest application due to its stability and compatibility with hydrophilic biopolymer chains (Fernandez-Cervera et al., 2004; Souza et al., 2013).

Guar-xanthan has been used as a stabilizer in starch-based biofilms in order to improve mechanical properties of polysaccharide biofilms. Xanthan gum is an extracellular polysaccharide obtained by aerobic fermentation of \textit{Xanthomonas campestris}. It has wide application in the food industry due to its ability to form viscous solutions at very low concentrations (Šuput et al., 2016). Beside xanthan gum, wide application also has guar gum with similar characteristics (Šuput et al., 2016). Guar gum acts as a thickening agent and stabilizer, helps maintaining structural homogeneity and functions as a binder (Šuput et al., 2016).

Although, addition of different additives can improve the flexibility and mechanical properties of biodegradable films, studies have shown that these additives can also have unwanted influence on some characteristics of films, especially on barrier properties. That is why it is very important to examine effect of appropriate plasticizers, stabilizers and other film’s additives and find their concentration for obtaining films with optimal performance for packaging of different food products with specific requirements.

The objective of this study was to examine influence of two additives in different concentrations on bi-layer film properties, and find optimal concentration of these additives that give film with best mechanical and barrier characteristics.

\section*{Materials and Methods}

The grounded hull-less pumpkin (\textit{Cucurbita pepo} L. ‘Olinka’) oil cake (PuOC) was stored at the temperature of 4°C. Other reagents used in this study were: glycerol (99.5%); guar-xanthan, zein, polyethylene glycol (PEG), ethanol (85%), and NaOH.

\subsection*{Preparation of bi-layer films}

The film-forming suspension of PuOC (10\%, w/w) in deionized water was produced with addition of glycerol (30\%, 40\%, or 50\% per weight of PuOC) and guar-xanthan (0.1\%, 0.3\%, or 0.5\% per weight of polysaccharides in PuOC). After adjusting pH = 12 using 0.2 M NaOH, and incubating at 90°C for 20 min and then filtrated through nylon filtrate, solutions were casted onto Teflon-coated Petri dishes and films were dried for 2 days at room conditions (23 ± 2°C, 50 ± 5% RH).

The film-forming solution of zein (Z) (10\% w/v) was prepared by suspending zein in 85\% ethanol with the addition of PEG 400 (50 \% w/w, per weight of zein), and incubating solution at 80°C. Zein solution was casted on dried PuOC films for obtaining composite bi-layer PuOC-Z films.

\subsection*{Film properties}

\subsubsection*{Thickness}

Film thickness was measured with a micrometer (Digico 1, Tesa, Swiss Made, Renens, Switzerland), with a sensitivity of 0.001 mm. The results were expressed as the mean of at least ten measurements on each film, from which an average was obtained.

\subsubsection*{Mechanical properties}

Tensile strength (TS, MPa) and elongation at break (EB, \%) of films were measured on an Instron Universal Testing Instrument Model No 4301 (Instron Engineering Corp., Canton, MA), according to the ASTM standard method D882-01.

The rectangular film strips of 80 mm in length and 15 mm in width were used. The initial grip separation was set at 50 mm, and crosshead speed was set at 50 mm/min. Tensile strength and elongation at break for each type of film was repeated at least three times, from which an average was obtained.

\subsubsection*{Physico-chemical properties}

Total soluble matter, moisture content and swelling of films were determined according to Hromiš et al. (2015). At least three measurements were conducted and average values were calculated with standard deviation (SD).

\subsubsection*{Barrier properties}

The \textit{water vapour transmission rate} (WVTR) was determined by the gravimetric method according to the standard ISO 2528:1995 (E). The used test conditions were: temperature 25°C ± 1°C; relative humidity 90\% ± 2%.

\textit{Determination of gas transmission rate} (CO\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}) was conducted in accordance with using isostatic gas-chromatographic method (DIN 53380, 1969), with the use of the Lyssy GPM-200 apparatus with the belonging Gasukuro Kogyo GC-320 gas chromatograph and the HP 3396A integrator.

The investigations were performed at 23°C and 1 bar pressure difference, and volume of sample (gas) injected was 0.8 ml. The results of transmission rate determination are expressed in ml/m\textsuperscript{2}/day at 1 bar pressure difference.

\section*{Results and Discussion}

\subsection*{Thickness}

Tested films had thickness from 0.26 mm to 0.33 mm. Slight increase of film average thickness was observed with increase of glycerol concentrations, for
the same concentrations of guar-xanthan. However, with increase of guar-xanthan concentration, for the same concentration of glycerol, slight decrease of film average thickness was obtained (Figure 1). Regardless of these slight differences, obtained results for thickness of all tested films were approximate 0.30 mm ± 10 %.

**Mechanical properties**

Mechanical properties – tensile strength (TS) and elongation at break (EB), of produced films are presented in figure 2.

The optimal mechanical properties, namely highest values for TS and EB, were determined for the film with 30% of glycerol and 0.5% of guar-xanthan. Obtained results showed that higher concentrations of glycerol (above 30%) led to decrease in TS end EB and formation of weak films. This is especially expressed for EB, where the films with minimum concentration of glycerol (30%) showed up to 5 times higher values than films with higher content of glycerol. Tapia-Blácido, Sobral and Menegalli (2005) obtained similar results. They examined the effect of drying temperature, relative humidity and concentration of glycerol on the mechanical properties of films based on Amaranth flour, and results showed that optimal mechanical properties could be obtained for similar conditions to the ones used in this experiment and 30% of glycerol concentrations (g/g dry matter). Maximal tested concentration of guar-xanthan (0.5%) gave films with highest TS as well as EB.

**Physico-chemical properties**

Physico-chemical properties of obtained films, such as moisture content, degree of swelling and total soluble matter, are presented in Figure 3. Obtained results are typical for biodegradable films, which, due to their hydrophilic nature, are very sensitive to moisture (Falguera et al., 2011; Han, 2014).

An increase of concentrations of guar-xanthan and glycerol had slight influence on increase of moisture content, as well as degree of swelling of films, while influence on total soluble matter wasn’t detected.

With increase of plasticizers concentration, due to their hydrophilicity, films probably absorb higher amount of water (Cho et al., 2002). Addition of hydrophilic substances, such as plasticizers, may also increase the degree of swelling of biodegradable films (Kavoosi et al., 2013).
Figure 3. Physico-chemical properties of obtained films – (a) moisture content, (b) degree of swelling and (c) total soluble matter

**Barrier properties**

Barrier properties, water vapor and gas transmission rate, are presented in Figures 4 and 5, respectively. Addition of selected additives had influence, not only on the mechanical properties, but also on barrier properties of obtained films. When WVTR is analysed, it can be seen that addition of highest concentrations of both additives, glycerol and guar-xanthan, led to increased WVTR (244.76 g/24h m²), while all other films showed WVTR in the range of (121.88÷180.22) g/24h m².

Incorporation of plasticizers may increase hydrophilicity of films, and, in this way, also increases WVTR (Chang et al., 2000; Wiles et al., 2000). Šuput et al. (2016) showed that incorporation of glycerol and guar-xanthan into starch-based films, also had negative effect on WVTR, increasing obtained values for starch films.

Gas transmission rate of tested films is presented in Figure 5. The results showed that all obtained films had very good barrier properties to O₂ (transmission rate lower than 50 ml/m²/day at 1 bar), regardless of concentrations of glycerol and guar-xanthan. Meanwhile, an increase of CO₂ transmission rate was observed with an increase of glycerol and guar-xanthan concentration. Results are in accordance with Popović et al. (2011) who produced biodegradable films based on PuOC (0.25 g/g PuOC of glycerol and without addition of guar-xanthan), and those films had very good gas barrier to O₂ (12.1 ml/m²/day at 1 bar) and CO₂ (42.2 ml/m²/day at 1 bar).
Conclusion

Obtained results showed that the optimal mechanical properties had film with the lowest concentration of glycerol and the highest concentration of guar-xanthan. Obtained values for moisture content, degree of swelling and total soluble matter are typical for biopolymer-based films and incorporated additives had minimal influence on these properties. Water vapor transmission rate of bi-layer film was altered only for highest concentrations of both additives. All tested films showed very good barrier to O2, which is one of the main require for food packing materials especially for very perishable products. With an increase of concentration of added substances, transmission rate of CO2 also increased. Presence of CO2 in packing may have an important role for maintaining the quality and extending the shelf-life of foods. However, for products for which process of respiration is characteristic, such as cheese, fresh fruits and vegetables, materials with higher transmission rate of CO2 can be advantageous.

References


Uticaj različite koncentracije glicerola i guar-ksantana na osobine dvoslojnog filma na bazi pogače uljane tikve golice i kukuruznog zeina

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Sažetak: Cilj ovog rada je da se ispita uticaj različite koncentracije glicerola i guar-ksantana na osobine dvoslojnog filma na bazi pogače uljane tikve (PuOC) i kukuruznog zena, kao i da se pronađe optimalna koncentracija ovih aditiva koja će dati filmove sa najboljim mehaničkim i barijernim osobinama. Različite koncentracije glicerola (30%, 40% i 50%) i guar-ksantana (0,1%, 0,3% i 0,5%) su dodate u PuOC sloj, dok je sastav zeinskog sloja ostao nepromenjen. Dobijeni rezultati pokazuju da najbolje mehaničke osobine ima film sa najmanjom koncentracijom glicerola (30%) i najvećom koncentracijom guar-ksantana (0,5%). Filmovi su pokazali lošiju barjeru prema vodenoj pari, a dobijene vrednosti su tipične za biopolimerne filmove. Međutim, svi ispitivani filmovi su pokazali veoma dobru barjeru za O₂ (brzina propustljivosti manja od 50 ml/m²/danu na 1 bar). Sa druge strane, sa povećanjem koncentracije dodatih aditiva, došlo je do povećanja brzine propustljivosti CO₂.

Ključne reči: biopolimeri, pogača uljane tikve, aditivi, dvoslojni filmovi, osobine

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