STRUCTURAL CHARACTERISATION OF STARCH BASED EDIBLE FILMS WITH ESSENTIAL OIL ADDITION

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ABSTRACT

Present study investigated structure of starch based edible films with essential oil addition. Films were obtained from water solutions containing gelatinized modified starch, polyol, guar-xantan gum modified mixture and essential oil by casting it on a Petri dish and evaporating at room temperature for 72h. Both, glycerol and guar-xantan modified mixture, had role to improve film flexibility and enable better film folding and handling. Two sample groups were obtained: starch based edible films with black cumin oil addition and starch based edible films with black pepper oil addition. Both essential oils were added in three different concentrations. Starch based edible film without essential oil addition was used as blank shot. Structural properties were determined by analyzing spectra obtained by FT-IR Spectrometer in the spectral range of 4000–400 cm^{-1} with a 4.0 cm^{-1} resolution. Software Omnic 8.1. and TQ Analyst were used to operate the FTIR spectrometer, collect and present all the data. Results pointed to quantitative law dependency between added amount of essential oils and spectra absorption values for both sample groups and FTIR spectra were used to calculate coefficient of correlation.

Keywords: packaging, edible films, starch, structural characteristics

1. INTRODUCTION

One of the matters of great concern nowadays is the environmental impact caused by the excessive quantity of non-degradable waste materials discarded every day. This reality has been stimulating research to develop new biodegradable packaging materials that could be considered environmentally friendly raw materials (Avérous et al., 2001). Among these materials, the ones derived from renewable resources, which participate in the carbon cycle, has received more attention since they combine environmental benefits and sustainability.

Edible films are thin layers of biopolymers that are used for the food packing. Edible films may be used to separate layers having different water activities retarding water transfer from one layer to the other (Guillard et al., 2003), may be a barrier for oxygen decreasing oil or fat oxidation, could be used as a barrier for oil uptake in deep fat frying (Holownia et al., 2000), used as a carrying agent for antimicrobial or functional substances (Han, 2002). Edible film coating with encapsulated antimicrobial substances can retard growth of microorganisms (Ko et al., 2001).

Several studies reported the use of starches from different sources to prepare films and coatings with different properties, and have indicated that these carbohydrates are promising materials in this regard (Avérous et al., 2001, Larotonda et al., 2005; Mali et al., 2005). Starch is one of the most frequently used biopolymer for edible films production due to the fact that could be obtained from large number of raw materials, its production costs are cheap, it is renewable and biodegradable biopolymer that has the ability to form films. Films developed from starch are described as isotropic, odourless, tasteless, colourless, non-toxic, biologically degradable, thus prevent a change of taste, flavor and appearance of food products (Chiumareli and Hubinger, 2012).

The main components of starch are linear amylose and highly branched amylopectin composed of glucose units via α-1,4 bonds (Blanshard, 1987). The ratio of amylose and amylopectin in the starch may affect starch behavior in processing and properties of the end product. They both consist of α(1–4) linked D-glucose units. Amylose is essentially linear, whereas amylopectin is a highly branched polymer due to 5–6% of α(1–6) links (Buleon et al., 1998). The native structure of starch is made of helices that are more or less radially organized forming a granule, which has to be described at different length scales. Some

structural aspects involving the arrangement of the molecules inside native starch granules and starchy materials are still matter of debate.

However, the application of starch films is restricted owing to the brittle nature (Imberty and Perez, 1988). The brittleness of starch materials is, among other things, mainly due to strong interactions between starch macromolecules (Takahashi et al., 2004), which may confine the polymeric segmental mobility (Muscat et al., 2011). Polymeric segmental mobility can be improved by doping some hydrophilic plasticizers, as a result of having interactions between plasticizer–starch instead of between starch–starch. Glycerol is one of the most popular plasticizers used in film-making techniques, due to stability and compatibility with hydrophilic bio-polymeric packaging chain (Fernandez Cervera et al., 2004).

The addition of essential oils and other components with antioxidant activity can improve functional properties of edible films and increase their potential use in the preservation of foods with a high fat content. Despite the great potential of essential oils, their use in food preservation remains limited mainly due to their intense aroma, toxicity problems and possible changes in the organoleptic properties of the food (Sanchez-Gonzalez et al., 2011). The use of edible coatings to carry essential oils could minimize the required doses by the encapsulation effect in the polymer matrix, which limits their volatilization and controls the compound release, thus reducing the negative impact of these ingredients.

The infrared spectroscopy, considering interactions at a local range order, has already been used to describe the organization and structure of starch films. The IR spectrum of starch has been shown to be sensitive to changes in molecular structure (short-range order), such as starch chain conformation, helicity, crystallinity and the retrogradation process as well as moisture content (Goodfellow & Wilson, 1990; Van Soest et al., 1995).

In this work, we investigated effect of essential oil addition on starch based film structural properties by using FR-IR spectroscopy method. FTIR spectra were used to make quantitative law dependency between added amount of essential oils and spectra absorption values for both sample groups to calculate coefficient of correlation.

2. MATERIALS AND METHODS

2.1. Materials
Film preparation: Starch films were prepared by casting aqueous starch solution. Aqueous solution of 2% (w/w) modified maize starch was prepared and heated at 90 ^{0}C for 60 minutes in a water bath. A weight of glycerol equal to 60% of the original starch was added and the solution was kept hot with mechanical stirring for 10 more minutes. Finally, guar-xantan modified mixture was added in a portion of 0.5% to initial starch weight. Guar-xantan modified mixture had role to enable better film folding and handling. Two different essential oils were added: black currant oil and black pepper oil in same concentrations in both cases: 0.5, 1 and 2% counted on mixture volume. Starch based edible film without essential oil addition was used as blank shot. The film-forming solution was homogenized using homogenizer at 10000 rpm for 1 min and then degassed under vacuum to remove dissolved air and then cast into Petri dishes. Each Petri dish was coated with 50 g of film forming solution on a leveled surface and left to dry at room temperature for 3 days.

Starch and guar-xantan modified mixture were kindly provided by "Palco" (Šabac, Serbia) and glycerol was purchased from „doo Laboratorija" (Novi Sad, Serbia).

2.1. Methods: Fourier transform spectroscopy

FTIR analysis of the film samples was carried out in the wave number range 4000 to 400 cm^{-1}, at a resolution of 4 cm^{-1}, using the IR spectrophotometer, Nicolet IS10, Thermo Scientific (Massachusetts, USA) and attenuation total reflection (ATR) extension. Each sample was scanned 32 times, while background shot was taken before the analysis of each sample. IR spectrophotometer is controlled via

computer equipped with software Omnic. Software Omnic 8.1. and TQ Analyst (Thermo Fisher Scientific, MA, USA) were used to operate the FTIR spectrometer, collect and present all the data.

3. RESULTS AND DISCUSSION

According to visual examination obtained films were transparent, odourless, easy to handle. It was proved that casting is adequate and easy process to produce films on a laboratory scale. Solvent is evaporated from the solution in order to form the film (Anker et al., 2001; Lazaridou and Biliaderis, 2002; Rindlav-Westling et al., 2002). Films were not greasy or sticky which means that amount of added plasticizer and guar xantan modified mixture was optimal. Previous research proved optimal concentrations (Šuput et al., 2013).
FTIR spectra may be used to define molecular interactions and some chemical components (Ferreira et al., 2009). An extremely broad peak appeared between 3000 and 3600 cm^{-1} centered at $3300cm^{-1}$. This is the region of hydrogen-bonded hydroxyl groups associated with free, inter- and intra- molecular bound hydroxyl groups (Haq et al., 2014). The peak occurring at 1641 cm^{-1} is associated with the tightly bound water present in the starch due to the hygroscopic nature of starch which is in agreement with findings of Zhang & Han, 2006. The peak at 1409 is related to the CH bending of CH_2. Peaks at 1240, 1299 and 1333 cm^{-1} are associated to OH bending due to the primary or secondary alcohols (Coates, 2000). Peaks at 2926, 1450 and 1370 cm^{-1} are ascribed to C-H stretching and bending modes which is in agreement with findings of Sheng et al., 2011. In two regions sample spectra show differences. First one is 1680 – $1770cm^{-1}$ which is presented in Fig 1. Generally, in spectral region 1800–1540 cm^{-1} starch doesn't absorb in it so the origin of these differences is from added oils. Based on IR spectral interpretation, samples with black cumin proved to have aliphatic ester groups: unsaturated groups at $1715cm^{-1}$ and alpha keto at $1745cm^{-1}$ while spectra of samples with black pepper had no peaks in this region. The other spectral zone where spectra differ is $2820-2980cm^{-1}$ which is shown at Fig 2. Based on IR spectral interpretation the CH_2 asymmetric stretching vibration occurs at at about 2930 cm^{-1} while symmetric CH_2 vibration occurs at 2870-2840 cm^{-1} for both group of samples but film samples with black cumin addition further have olefin functional group. Functional group is detected as C-C Stretching Vibrations and C-H Stretching and Deformation Vibrations.
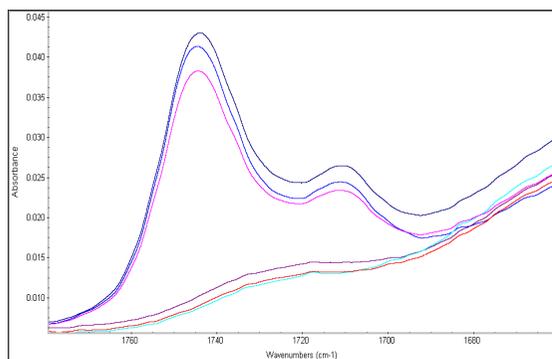
Figure 1 Differences in spectral region 1680-1760cm^{-1}
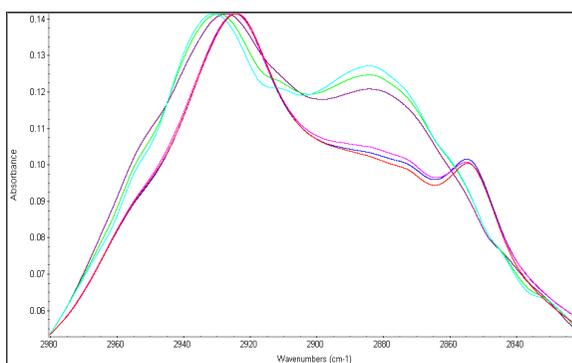
Figure 2 Differences in spectral region 2840-2980cm^{-1}

Using software TQ Analyst, quantitative analysis Simple Beer's law was performed on spectra of starch based edible films with growing amount of two different essential oils: black cumin and black pepper. Functional dependency, described by equation:

$$y=(0.709e\text{-}3)x+(\text{-}0.230e\text{-}3) \tag{1}$$

was determined between the amount of added black cumin essential oil and the FTIR spectra of starch based edible films with growing amount of oil, in the spectral region of 3275.50-3281.29cm^{-1}. Calculated versus actual values showed very good correlation (R^2=0.99617) for the linear function.

Functional dependency, described by equation:

$$y = (-0.459e\text{-}3)x + (0.856e\text{-}3) \tag{2}$$

was determined between the amount of added black pepper essential oil and the FTIR spectra of starch based edible films with growing amount of oil, in the spectral region of 3275.50-3281.29cm^{-1}. Calculated verses actual values showed very good correlation (R^2= 0.99321) for the linear function.

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