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EFFECT OF BLACK CUMIN OIL ON MECHANICAL AND STRUCTURAL CHARACTERISTICS OF STARCH BASED EDIBLE FILMS

EFEKAR ULJA CRNOG KIMA NA MEHANIČKE I STRUKTURNE OSOBINE JESTIVIH FILMOVA NA BAZI SKROBA

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ABSTRACT

The main goal in this work was to investigate the structure of starch based edible films with essential oil addition. Films were obtained from water solution containing starch, polyol, guar-xantan gum modified mixture and essential oil by casting it on a Petri dish. Black cumin essential oil was added in three different concentrations. Starch based edible film without essential oil was used as a control. Physical, mechanical and structural properties are determined: thickness, tensile strength, elongation at break and film structure. FTIR results pointed to quantitative law dependency between amount of essential oil and spectra absorption values. Based on dependency coefficient of correlation was calculated (R^2=0.99483).

Key words: *packaging, edible films, starch, essential oil.*

REZIME

Glavni cilj rada je ispitivanje strukture jestivih filmova na bazi skroba kojima je dodato etarsko ulje. Filmovi su dobijeni iz vodenog rastvora, koji sadrži skrob, poliol, guar-ksantan modifikovanu smešu i etarsko ulje, razlivanjem na Petri ploči. Etarsko ulje crnog kumina je dodato u tri različite koncentracije. Jestivi skrobni film kojem nije dodato esencijalno ulje je korišćen kao kontrola. Fizičke, mehaničke i strukturne osobine su određene: debljina, zatezna jačina, izduženje pri kidanju i struktura filma. FTIR rezultati su dokazali kvantitativnu zavisnost između dodate količine etarskog ulja i vrednosti apsorpcije spektara. Na osnovu ove zavisnosti izračunat je koeficijent korelacije (R^2=0,99483).

Ključne reči: *ambalaža, jestivi filmovi, skrob, etarsko ulje.*

INTRODUCTION

Recently, environmentally friendly materials based on natural and renewable resources have received much attention (*Davis and Song, 2006; Marsh and Bugusu, 2007; Ma and Yu, 2004; Nakamura et al., 2005; Yu et al., 2006*) for their eco-friendly status in opposition to plastics (*Lazić et al., 2013*). Starch, as an abundant raw material with low cost, has been applied in the field of degradable plastics, and blend films containing starch are potential materials in the agriculture, medicine, and packaging industries (*Lu et al., 2005*). Starch is one of the most preferred green packaging materials due to its rapid biodegradable nature, having renewable source, availability in relatively low cost and production at low cost and on large scale (*Parra et al., 2004; Liu et al., 2011; Majdzadeh-Ardakani et al., 2010; Nejad et al., 2011; Qiao et al., 2010*). Starch and modified starches are widely used as food packaging materials (*Avella et al., 2005*), coatings (*Fringant et al., 1998*), and textile sizing agents (*Mostafa & El-Sanabary, 1997*).

In plants, starch is organised into structurally complex granules. Despite variations in composition, size and shape, a general description of the starch granule organisation is commonly accepted (*Donald et al., 1997*). Starch granules can be considered as a combination of two components, amylose and amylopectin. They both consist of a (1–4) linked D-glucose units. Amylose is essentially linear, whereas amylopectin is a highly branched polymer due to 5–6% of a(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. The infrared spectroscopy, considering interactions at a local range order, has already been used to describe the organization and structure of starch. The development of sampling devices like attenuated total reflectance (ATR) Fourier transform infrared (FTIR) combined with procedures for spectrum deconvolution provide opportunities for the study of starch structure. ATR-FTIR is a surface analytical method that can acquire information on the outer region of a sample.

Modified starches have been approved for food use, in which they act as thickeners, gelling agents, as sizing agents in textiles and as adhesives for paper and paper products. The application of starch-based films in food packaging is promising because of their environmental appeal, low cost, flexibility and transparency (*Müller et al., 2009; Bilbao-Sáinz et al., 2010*). Edible films made from starch are tasteless, odorless and transparent, thus prevent a change of taste, flavor and appearance of food products (*Chiumareli and Hubinger, 2012*). Main advantages of starch films are excellent barrier properties to O_2 and CO_2, on the other hand it has weaker barrier properties to the water due to high hydrophilicity (*Šuput et al., 2013*).

Functional foods, enriched in biologically active compounds are becoming increasingly available in many countries and the potential markets are enormous. 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 (*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.

In this work, we investigated the effect of black cumin essential oil addition on mechanical and structural properties of starch based films.

MATERIAL AND METHOD

Reagents

Starch and guar-xantan modified mixture were kindly provided by Palco (Šabac, Serbia). Essential oils were obtained from Probotanic (Belgrade, Serbia) and glycerol was obtained from Laboratorija doo (Novi Sad, Serbia).

Film preparation

Starch films were prepared by casting aqueous starch solution. Aqueous solution of 2% (w/w) maize starch was prepared and heated at 90 ^{0}C for 60 minutes in a water bath. A weight of glycerol equal to 50% 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 0.3% to initial starch weight. Guar-xantan modified mixture had role to enable better film folding and handling. Black cumin essential oil was added in three different concentrations: 0.5, 1 and 2% counted on mixture volume. Starch based edible film without essential oil addition was used as a control. 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 film forming solution on a leveled surface and left to dry at room temperature.

Mechanical properties

Film thickness was measured using a micrometer with sensitivity of 0.001 mm. Ten thickness measurements were carried out on each film, from which an average was obtained.

Tensile strength (TS) 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 ASTM standard method D882-01. A rectangular film strip of 80 mm in length and 15 mm in width was used. The initial grip separation was set at 50 mm, and crosshead speed was set at 50 mm/min. The TS and EB of the strips were measured in a static mode. EB was calculated as the percent of change by dividing film elongation at the moment of rupture by initial gage length of the specimen (50 mm) and multiplying by 100. TS and EB measurements for each type of film were repeated 10 times, from which an average was obtained.

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.

Statistical analysis

Descriptive statistical analyses for calculating the means and the standard error were performed using MicroSoft Excel software (MicroSoft Office 2007). All obtained results were expressed as the mean ± standard deviation (SD).

RESULTS AND DISCUSSION

According to visual examination obtained films were transparent, odourless, easy to handle. Films were not greasy or sticky which means that amount of added plasticizer and guar xsantan modified mixture was optimal. It was proved that casting was adequate and easy process to produce films on a laboratory scale. Solvent was evaporated from the solution in order to form the film (*Anker et al., 2001; Lazaridou and Biliaderis, 2002; Rindlav-Westling et al., 2002*). Film thickness was in the range 0.161 to 0.166 mm. Appropriate film formation contributed to uniform film thickness no matter the amount of added essential oil (Table 1). Very small values of standard deviation proved film uniformity, no matter it is biologically active material.

Table 1. Starch based edible films thickness with different amount of added essential oil (mm) (mean ± SD): 0 – blank shot film, A – 0.5% oil, B – 1% oil , C – 2% oil

	Control	A	B	C
Thickness	0.161±0.004	0.166±0.009	0.165±0.006	0.162±0.005

Results related to mechanical properties are shown in Fig. 1a and Fig. 1b. Tensile strength values of tested films were in the range 0.051 to 0.0702 N/15mm, while TS value of blank shot was 0.1828 N/15mm. Fig 1a. shows that black cumin essential oil addition increased TS values which is in accordance of *Souza (2013)* findings. Elongation at break values of tested films were in the range 36,996 to 52,308%, while EB value of blank shot was 7,67%. Fig 1b. shows that black cumin essential oil addition increased EB values which is in accordance of *Ghasemlou (2014)* findings.

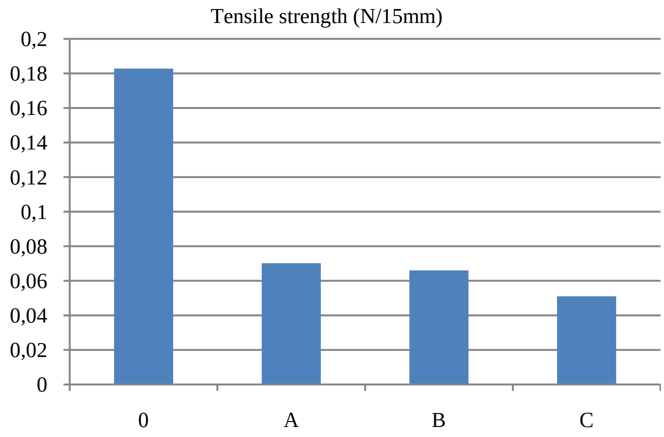

Fig. 1a. Tensile strength of films with different oil concentration (N/15mm): 0 – blank shot film, A – 0.5% oil, B – 1% oil , C – 2% oil

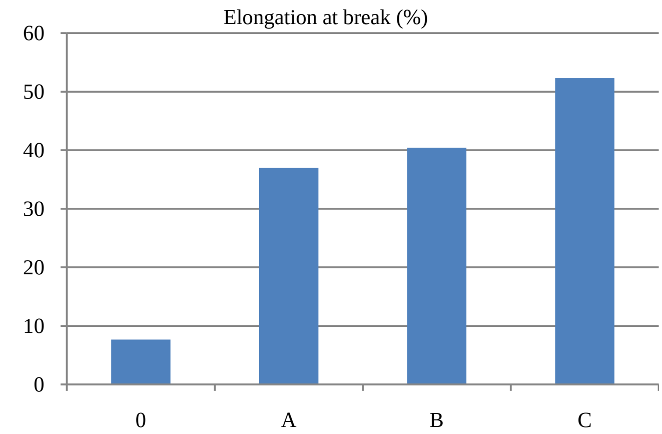

Fig. 1b. Elongation at break of films with different oil concentration (%): 0 – blank shot film, A – 0.5% oil, B – 1% oil, C – 2% oil

FTIR spectra may be used to define molecular interactions and some chemical components (*Ferreira et al., 2009).* Figure 2 shows spectra obtained by using FTIR spectroscopy in the spectral range 4000 to 400 cm^{-1}. It could be concluded that starch structure dominates regarding molecular interaction presented in Figure 2 since spectra with essential oil addition and blank shot spectrum (with no added oil) are similar.

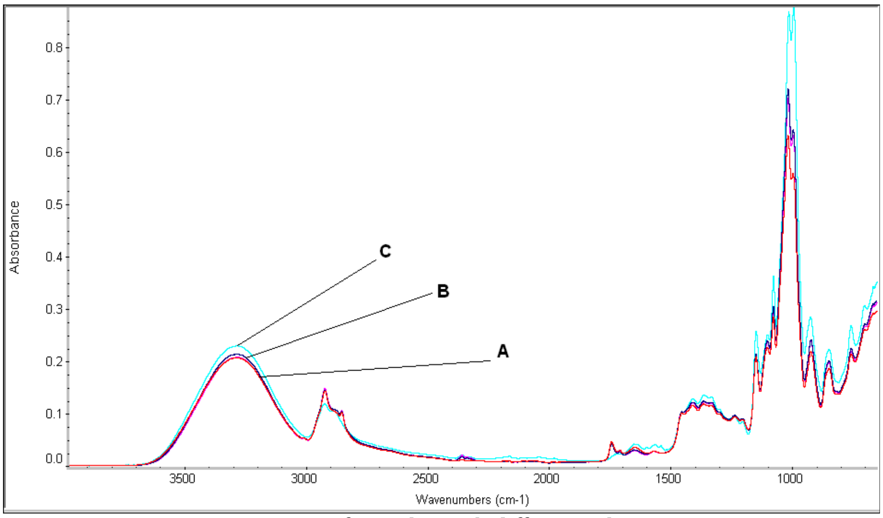

Fig. 2. FTIR spectra of samples with different oil concentration: A – 0.5% oil. B – 1% oil. C – 2% oil

Since starch doesn't absorb in spectral region 1800-1540 cm^{-1} (*Demiate et al., 2000*) molecular interactions of added oil could be found in that region and they are aliphatic ester groups: unsaturated groups at 1715 cm^{-1} and alpha keto at 1745 cm^{-1}, which are shown in Figure 3. Also samples with black cumin addition have olefin functional group detected as C-C and C-H stretching vibrations.

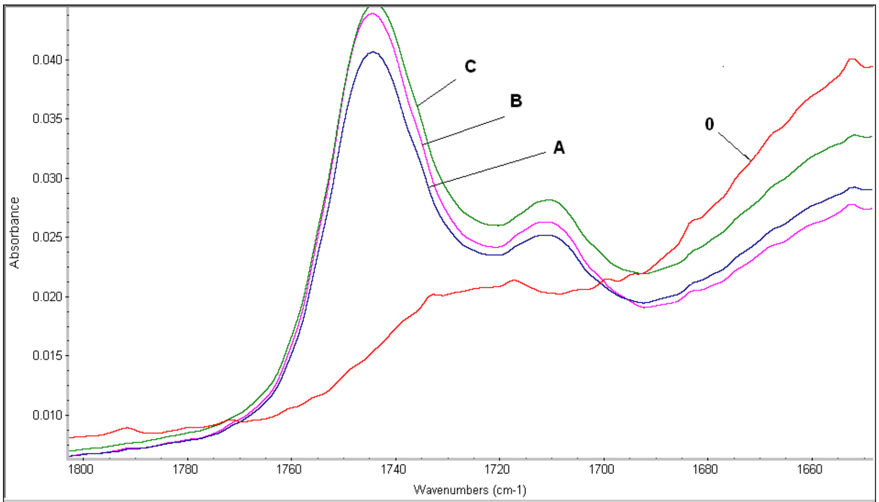

Fig. 3. Essential oil interactions in spectral region 1650 -1800 cm^{-1}: 0 – blank shot film, A – 0.5% oil, B – 1% oil , C – 2% oil

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

$$y=(0.711e-3)x+(-0.208e-3) \quad (1)$$

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. Calculated verses actual values are shown in Table 2 and showed very good correlation (R^2=0.99483) for the linear function.

Tab. 2. Calculated verses actual values by using Simple Beer's law

Index	Spectrum title	Actual	Calculated
1	0	0	0
2	A	0.5	0.53
3	B	1	0.98
4	C	2	2.06

CONCLUSION

Obtained starch based edible films with essential oil addition films were transparent, odourless, strong and flexible. Film thickness uniformity (0.161 to 0.166 mm) proved that casting is adequate and easy process to produce films. Essential oil addition affected film mechanical characteristics. Tensile strenth and elongation at break values increased (0.051 N/15 mm to 0.0702 N/15 mm and 36.996% to 52.308%, respectively) as black cumin essential oil was added. Regarding structural characteristics, spectra were taken and apsorbance where starch doesnt absorb was evaluated. Based on IR spectral interpretation, molecular interactions of aliphatic ester groups and olefin functional groups were detected. FTIR spectra were useful tool to make quantitative law dependency between added amount of essential oils and spectra absorption values. Coefficient of correlation (R^2=0.99483) was calculated.

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