

## EFFECT OF PROCESS PARAMETERS ON BIOPOLYMER FILMS BASED ON SUNFLOWER OIL CAKE

### UTICAJ PROCESNIH PARAMETARA NA OSOBINE BIOPOLIMERNIH FILMOVA NA BAZI POGAČE SUNCOKRETA

Danijela ŠUPUT, Vera LAZIĆ, Senka POPOVIĆ, Nevena HROMIŠ, Sandra BULUT, Lato PEZO, Jovan BANIĆEVIĆ  
Faculty of Technology, University of Novi Sad, 21000 Novi Sad, Bulevar Cara Lazara 1, Serbia  
e-mail: suput.danijela@gmail.com

#### ABSTRACT

The purpose of this paper is the synthesis and characterization of biodegradable composite films based on whole sunflower oil cake, as well as the effect of process parameters (pH and temperature) on the film properties obtained. Films were synthesized at different temperatures (room temperature, 60 °C and 90 °C) and pH values (10 and 12). The film samples obtained were characterized by the mechanical, barrier and physicochemical properties determination. The experimental results showed that the tensile strength values increased with temperature and pH value increments, whereas the sample with the highest elongation at break value was 60 °C/pH12. The water vapour permeability values were uniform (8.62 g/m<sup>2</sup>h - 11.63 g/m<sup>2</sup>h), and lower values were recorded in samples synthesized at higher temperatures. The results obtained relative to light transmission were uniform, and the maximum transmission value was reached at 800 nm (24.1- 35.7 %). The values obtained for swelling and solubility parameters are characteristic of the nature of biopolymer films.

**Keywords:** biopolymers, sunflower oil cake, process parameters, characterization.

#### REZIME

Obnovljive sirovine i agroindustrijski otpad su odlične sirovine za sintezu biorazgradivih polimera zbog široke rasprostranjenosti, niske cene i jednostavnosti prerade. Nusproizvodi industrije prerade ulja su pogodne sirovine za proizvodnju biopolimernih ambalažnih materijala zbog visokog sadržaja proteina. Dosadašnja brojna istraživanja pokazala su da proteini suncokreta imaju odlične sposobnosti za formiranje proteinskih filmova iz izolata pogače. Cilj ovog rada je sinteza i karakterizacija biorazgradivih kompozitnih filmova na bazi celokupne pogače suncokreta. U radu su prikazani rezultati ispitivanja uticaja procesnih parametara pH-vrednosti i temperature na osobine dobijenih filmova. Filmovi su sintetisani na različitim temperaturama: sobna, 60°C i 90°C i pri pH vrednostima 10 i 12. Dobijeni uzorci filmova okarakterisani su određivanjem mehaničkih, barijernih i fizičko-hemijskih osobina. Dobijeni rezultati pokazuju da su povećanjem vrednosti temperature i pH rastle i vrednosti zateznih jačina, dok je uzorak sa najvećim izduženjem pri kidanju bio 60°C/pH12. Vrednosti propustljivosti vodene pare su ujednačene i kreću se u opsegu 8,62-11,63 g/m<sup>2</sup>h, a niže vrednosti se uočavaju kod uzoraka sintetisanih na višim temperaturama. Prilikom određivanja propustljivosti svetlosti, uzorci se ponašaju ujednačeno i maksimalnu vrednost transmisije dostižu na 800 nm (vrednosti se kreću od 24,1% do 35,7%). Dobijene vrednosti za bubrenje i rastvorljivost su karakteristične za prirodu biopolimernih filmova. Na osnovu dobijenih rezultata karakterizacije filmova može se zaključiti da su optimalni procesni parametri za sintezu biopolimernih filmova od celokupne pogače suncokreta - temperatura 90°C i pH-vrednost 12.

**Ključne reči:** biopolimeri, pogača suncokreta, procesni parametri, karakterizacija.

#### INTRODUCTION

Most preferable packaging methods at present are those exerting the least impact on the environment due to growing environmental issues in the world. As a good substitute for conventional packaging material, i.e. plastics, biodegradable materials isolated from renewable sources and agro-industrial waste have been studied (Lazić and Novaković, 2010, Šuput et al., 2017). Agro-industrial wastes in the form of oil cakes, the residues of the edible vegetable oil production, contain a large amount of protein and thus are mainly used as foods for various animal species. Due to their high protein content, oil cakes can be used for obtaining isolated components (Ramachandran et al., 2007). Components isolated from agro-industrial waste form films with good characteristics, including barrier and adhesive properties as well as resistance to oils and organic solvents (De Graaf et al., 2001; Nesterenko et al., 2013).

In this paper, biofilms obtained from sunflower cake were examined. Sunflower oil cake (SFOC) is defined as a by-product that occurs in the pressing and extraction of sunflower seed during oil production (Rincon et al., 2011). Sunflower oil cake

presents sunflower seeds without oil components. Previous studies have shown that sunflower cake is rich in proteins (containing more than 30 % of protein) (Ayhllon-Mixueiro et al., 2000). The usual composition of the SFOC is presented in Table 1 (Geneau-Sabtraoï et al., 2008).

Proteins are predominant in sunflower oil cake, followed by cellulose and hemicellulose (Geneau-Sabtraoï et al., 2008). Proteins that build biopolymer films have good pseudoplastic and viscoelastic properties, as well as thermal properties that are similar to the thermal properties of synthetic polymers (Geneau-Sabtraoï et al., 2008). The application of sunflower oil cake as a raw material for the production of biopolymer films is limited due to the presence of phenolic components, especially chlorogenic and caffeic acid, which affect the quality of sunflower oil cake proteins (Nesterenko et al., 2013).

The purpose of this paper is the synthesis and characterization of biodegradable composite films based on whole sunflower oil cake. The effect of process parameters on the properties of the films obtained (pH and temperature) was examined. The films obtained were synthesized at temperatures of 25 °C, 60 °C and 90 °C, as well as pH values of 10 and 12. These parameters are based on previous research (data not

shown). The films obtained were characterized by determining their mechanical, physicochemical, barrier and structural properties.

Table 1. Chemical composition of sunflower oil cake (Orliac et al., 2002; Rouilly et al., 2006)

Components	Content (%)
Ligno-cellulose fibers	37.3
Cellulose	22.3
Lignin	5.2
Hemicellulose	9.8
Proteins	35.6
Globulins	55-60
Albumins	17-23
Glutelins	11-17
Prolamins	1-4
Minerals	7.6
Phenol compounds	5.7
Lipids	1.0
Water	10.0
Ash	7.6

## MATERIAL AND METHOD

### Film synthesis

For the purpose of the biopolymer film synthesis, whole sunflower oil cakes were used with the addition of glycerol (10 %) as a plasticizer, followed by the adjustment of the pH value to 10 and 12 with sodium hydroxide solution addition. After the pH adjustment, the temperature was adjusted by heating in a water bath. The samples were kept at 25 °C, 60 °C and 90 °C for 20 minutes with stirring. The resulting film forming solution was filtered through a filtration fabric and the filtrate was cast onto Teflon-coated glass surfaces, where the drying of the films was carried out at room temperature for 5 days.

### Methods

Firstly, films were **visually examined** and described.

**Film thickness** was measured using a micrometer (type 30, Tesa, Switzerland) with a sensitivity of 1 µm. Thickness measurements were carried out on each film at 8 different positions.

### Mechanical properties

Tensile strength (TS) and elongation to break (EB) were measured using the Instron Universal Testing Instrument Model No 4301 (Instron Engineering, Canton, Massachusetts, USA), according to the standard method EN ISO 527-3:1995. The film samples were cut into rectangular strips (15x80 mm). The initial grip separation was set at 50 mm, and the crosshead speed was set at 50 mm/min. TS and EB measurements for each sample were repeated eight times.

**Water vapor permeability** was determined by the standard gravimetric method ISO 2528:1995. A biopolymer film sample was applied to the vessel containing the desiccant -silica gel, and then the system was deposited in a desiccator (the relative air humidity was set to 90 % and the temperature was in the range of 23 ± 2 °C). Water vapor permeability is expressed as the ratio of the difference between the mass of the desiccant before and after a certain time, i.e. after the absorption of moisture. The difference in mass was measured every hour using an analytical balance.

**Light permeability** was determined by the analytical instrument technique - spectrophotometry in UV and visible spectrum (in the wavelength range of 200-800 nm).

**Moisture content** was determined as a percentage of weight reduction during film drying at 105 °C against the total weight of the film:

$$MC (\%) = 100 [(m_2 - m_1) - (m_3 - m_1)] / (m_2 - m_1)$$

where  $m_1$  - mass of measuring vessel,  $m_2$  - mass of film samples with measuring vessel prior to drying;  $m_3$  - mass of dried film samples with a measuring vessel

### Film swelling

Film samples (1x2 cm) were weighed ( $m_1$ ) and subsequently dipped in deionized water at room temperature for 2min. Finally, the samples were removed from water (the excess water was removed by a filter paper) and weighed ( $m_2$ ). The swelling degree was calculated as follows:

$$\text{Swelling (\%)} = 100 (m_2 - m_1) / m_1$$

where  $m_1$  - mass of film samples prior to dipping in deionized water,  $m_2$  - mass of film samples after dipping in deionized water

### Film solubility

After moisture content determination, dry film samples were immersed in deionized water at room temperature for 30 min with hand stirring. After 30 min, the excess water was decanted and the samples were dried in the oven at 105 °C for 60 min (prior to their weighing ( $m_4$ )). The solubility of the films examined in water was calculated as follows:

$$\text{Solubility (\%)} = 100 [(m_3 - m_1) - (m_4 - m_1)] / (m_3 - m_1)$$

where  $m_1$  is the mass of measuring vessel,  $m_2$  is the mass of film samples with measuring vessel prior to drying,  $m_3$  is the mass of dried film samples with a measuring vessel, and  $m_4$  is the mass of dried film samples with a measuring vessel after immersion and drying.

Five repetitions were performed in examining the moisture content, film swelling and film solubility of each sample.

### Statistical analysis

All data were presented as mean values with their standard deviation indicated (mean ± SD). Furthermore, the analysis of variance (ANOVA) was performed using the post-hoc Tukey's HSD test.

## RESULTS AND DISCUSSION

A visual examination indicated that the color of the synthesized films ranged from brown to dark shades of green, depending on the process parameters. The films obtained are non-transparent and thin. They are uneven with a smooth side in contact with the non-adhesive Teflon surface, where the films were cast.

The results of the mechanical properties examination are shown in Table 2. The film thickness varied in the range from 0.054mm to 0.087 mm. The pH and temperature values do not significantly alter the film thickness.

Basic indicators of packaging material mechanical properties are tensile strength (TS) and elongation at break (EB). The samples synthesized at higher temperatures and higher pH values showed higher values of tensile strength. The sample casted at temperature of 90 °C and the pH value 12 had the highest tensile strength. The optimum elongation at break was achieved for samples at a temperature of 60 °C and a pH value of 12. Regardless of the results obtained, no clear relationship between the temperature and the mechanical properties was noticed. However, a pH value of 12 was found to provide the optimum

tensile strength and elongation at break values for the materials tested.

Table 2. Mechanical properties of composite films obtained from sunflower oil cake at different process parameters

Process parameter t°C /pH	Thickness (mm)	Tensile strength (MPa)	Elongation at break (%)
Room temp/pH 10	0.065±0.002 <sup>b</sup>	1.58±0.015 <sup>a</sup>	12.67±2.257 <sup>a</sup>
Room temp/pH 12	0.087±0.008 <sup>e</sup>	2.07±0.16 <sup>b</sup>	17.46±1.43 <sup>b</sup>
60°C /pH 10	0.054±0.006 <sup>a</sup>	2.73±0.22 <sup>c</sup>	18.04±3.87 <sup>b</sup>
60°C /pH 12	0.068±0.001 <sup>c</sup>	3.12±0.25 <sup>d</sup>	37.23±3.368 <sup>d</sup>
90°C /pH 10	0.075±0.006 <sup>d</sup>	1.76±0.08 <sup>a</sup>	16.21±2.87 <sup>b</sup>
90°C /pH 12	0.074±0.011 <sup>d</sup>	4.37±0.23 <sup>e</sup>	22.03±4.86 <sup>c</sup>

\*Different letters written in superscript within the same column in the table show significantly different means of the data observed (at  $p < 0.05$  level) ( $n = 3$ ).

The results relative to water vapor permeability are shown in Figure 1. The results obtained are uniform (ranging from 8.62 g/m<sup>2</sup>h to 11.63 g/m<sup>2</sup>h) and characteristic of biopolymer films.

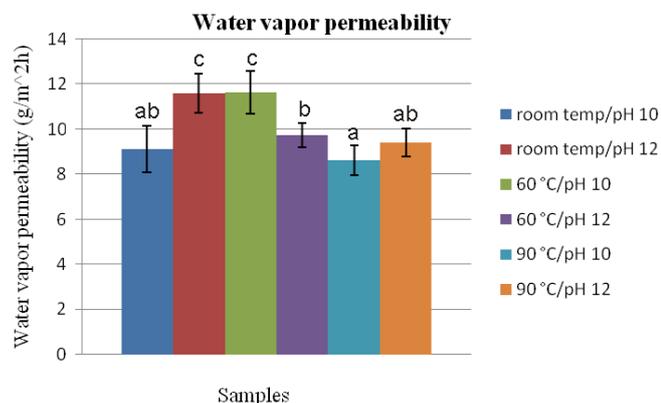


Fig. 1. Water vapor permeability (g/m<sup>2</sup>h) of composite films obtained from sunflower oil cake at different process parameters

\*Different letters written in superscript within the same column in the table show significantly different means of the data observed (at  $p < 0.05$  level) ( $n = 3$ ).

The results obtained by measuring the light permeability show that all the biopolymer films tested have transmittance values of less than 1 % at wavelengths between 200 nm and 400 nm. As they are in the UV spectral range, synthesized biopolymers are good light barriers and can be used as packaging materials for the UV light sensitive products. Figure 2 shows the transmission values for a series of samples of biopolymer films in the range of 400 nm to 800 nm.

On the basis of the light permeability measurements performed, it can be concluded that all the samples provide equal barriers to light until approximately 650 nm. Each of the samples reached maximum permeability at a wavelength of 800 nm. The final transmission values ranged from 24.1 % to 35.7 %.

The experimental results relative to the physicochemical properties measured (namely moisture content, swelling degree and solubility) are shown in Table 3. The moisture content values obtained are uniform (ranging from 13.76 % to 20.47 %), and the samples prepared at a pH value of 10 retain a higher amount of moisture compared to the samples prepared at a pH value of 12, regardless of temperature values.

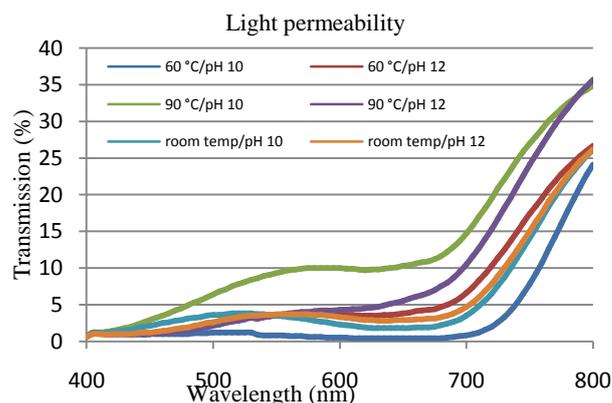


Fig. 2. Transmission (%) of composite films obtained from sunflower oil cake at different process parameters

Table 3. Moisture content of composite films obtained from sunflower oil cake at different process parameters

Process parameter t°C /pH	Moisture content (%)
Room temp/pH 10	20.47±1.68 <sup>d</sup>
Room temp/pH 12	17.42±1.23 <sup>b</sup>
60°C /pH 10	20.07±1.89 <sup>d</sup>
60°C /pH 12	17.34±2.71 <sup>b</sup>
90°C /pH 10	19.05±5.17 <sup>c</sup>
90°C /pH 12	13.76±2.46 <sup>a</sup>

\*Different letters written in superscript within the same column in the table show significantly different means of the data observed (at  $p < 0.05$  level) ( $n = 3$ ).

Film solubility and swelling are connected with water diffusion, the ionization of the carboxyl and amino groups, the dissociation of hydrogen and ionic bonds and the relaxation of the polymer in the presence of moisture (Mathew et al., 2006). The swelling degree and solubility values obtained for the biopolymer films examined are shown in Figure 3 and 4.

Swelling is an important physicochemical characteristic of sunflower oil cake. It has been found that the swelling of sunflower oil cake increases with an increase in the alkalinity of the solution due to the increase in the cellulose fiber volume and the ionization of proteins in the alkaline environment (Isogai et al., 1992). When the temperature increases from 50 °C to 150 °C, the mass loss of sunflower oil cake occurs due to the dehydration of its components. The components of sunflower oil cake are not stable at temperatures ranging from 190 °C to 220 °C.

The solubility of sunflower oil cake is minimal at the isoelectric point (pH = 4.5). Increasing solubility could be achieved in acid and alkaline environments on account of the balance distortion between protein-solvent and protein-protein interactions (Mo et al., 2006). Negative groups (COO<sup>-</sup> groups) are present at higher pH values, whereas positive groups (NH<sub>3</sub><sup>+</sup>) are present at lower pH values, which leads to polymer chains rejection and solubility increase (Fennema, 1993).

On the basis of the results obtained, it could be argued that the solubility values of all the biopolymer films examined are less than 40 %, which consistent with previous studies (Nguyen, 2012). Moreover, films synthesized at higher pH values (12) exhibited higher solubility values compared to those produced at a pH of 10.

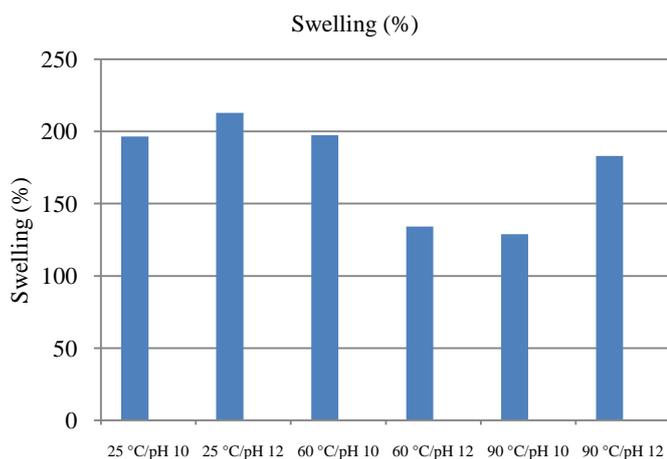


Fig. 3. Swelling degree (%) of composite films obtained from sunflower oil cake at different process parameters

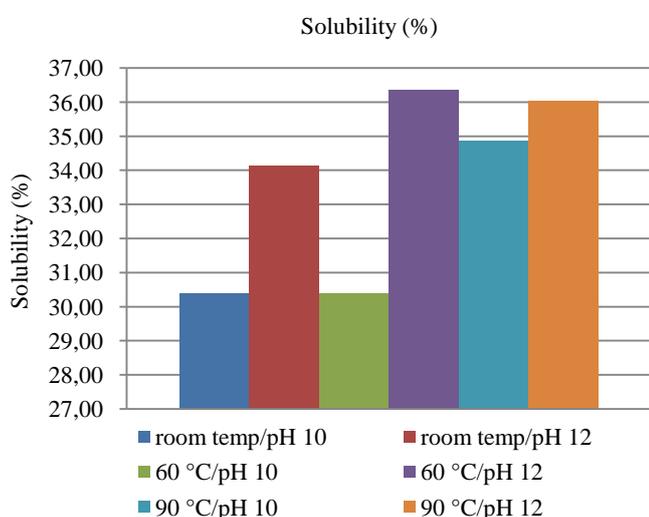


Fig. 4. Solubility (%) of composite films obtained from sunflower oil cake at different process parameters

## CONCLUSION

The present study confirms the possibility of using whole sunflower oil cake as a raw material for the synthesis of biopolymer films under laboratory conditions using the procedures argued herein. The biopolymer films obtained are dark and shiny, featuring favorable tactile characteristics (smooth, flexible) and sunflower fragrance. On balance, their properties, with minor deviations, are characteristic of biopolymer films. Based on the effect of process parameters on the properties of biopolymer films obtained from sunflower oil cake, the optimal process conditions for the synthesis of films with enhanced features can be argued. As it is essential that films be firm but flexible (with low water vapor and light transmission, as well as lowest possible moisture content and solubility/swelling degree) further investigation will be conducted involving films obtained at 90 °C and a pH value of 12. The data obtained can provide a basis for further research in order to utilize biopolymer materials synthesized from whole sunflower oil cake in the production of commercial packaging materials.

**ACKNOWLEDGEMENT:** This paper is part of the project TR-31055, financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

## REFERENCES

- Ayhllon-Meixueiro, F., Vaca-Garcia, C., Silvestre, F. (2000). Biodegradable films from isolate of sunflower (*Helianthus annuus*) proteins. *Journal of Agricultural and Food Chemistry*, 48,3032-3036.
- De Graaf, L.A., Harmgen, P.F.H., Vereijken, J.M., Monikes, M. (2001). Requirements for nonfood applications for pea proteins – A review. *Nahrung/Food*, 45(6), 408-411.
- Fennema, O. R. (1993). *Food Chemistry*. New York, United States: Marcel Dekker Inc.
- Geneau-Sabtraoi, C., Leyris, J., Silvestre, F., Rigal, L. (2008). Sunflower cake as a natural composite: composition and plastic properties. *Journal of Agricultural and Food Chemistry*, 56(23), 11198-11208.
- Isogai, A., Onabe, F., Usuda, M. (1992). Swelling behaviour of cellulose by chemical and mechanical treatments. *Journal of the Society of Fiber Science and Technology, Japan*, 48(9), 487-492.
- Lazić, V., Novaković, D. (2010). *Ambalaža i životna sredina*, University of Novi Sad, Novi Sad, Serbia.
- Mathew, S., Brahmakumar, M., Abraham, T. E. (2006). Microstructural imaging and characterization of the mechanical, chemical, thermal, and swelling properties of starch- chitosan blend films. *Biopolymers*, 82(2), 176-187.
- Mo, X., Zheng, Z., Wang, D., Sun, X. (2006). Soybean glycinin subunits. Characterization of physicochemical and adhesion properties. *Journal of Agricultural and Food Chemistry*, 54(20),7589-7593.
- Nesterenko, A., Alric, I., Violleau, F., Silvestre, F., Durrieu, V. (2013). A new way of valorizing biomaterials: The use of sunflower proteins for alpha-tocopherol microencapsulation. *Food Research International*, 53(1), 115-124.
- Nguyen, M.X.H. (2012). Characterization of allergenic and antimicrobial properties of chitin and chitosan and formulation of chitosan-based edible film for instant food casing. School of Applied Sciences. RMIT University, Melbourne, Australia.
- Orliac, O., Rouilly, A., Silvestre, F., Rigal, L. (2002). Effects of additives on the mechanical properties, hydrophobicity and water uptake of thermo-moulded films produced from sunflower protein isolate. *Polymer*, 43(20), 5417-5425.
- Ramachandran, S., Singh, S. K., Larroche, C., Soccol, C. R., Pandey, A. (2007). Oil cakes and their biotechnological applications – A review. *Bioresource Technology*, 98(10), 2000-2009.
- Rincon, B., Portillo, M. C., Gonzáles, J. M., Fernández-Cegrí, V., Ángeles de la Rubia, M., Borja, R. (2011). Feasibility of sunflower oil cake degradation with three different anaerobic consortia. *Journal of Environmental Science and Health, Part A: Toxic/hazardous Substances and Environmental Engineering*, 46(12), 1409-1416.
- Rouilly, A., Orliac, O., Silvestre, F., Rigal, L. (2006). New natural injection-moldable composite material from sunflower oil cake. *Bioresource Technology*, 97(4), 553-561.
- Šuput, D., Lazić, V., Popović, S., Hromiš, N., Bulut, S. (2017). Biopolymer film synthesis and characterization. *Journal on Processing and Energy in Agriculture*, 21(1), 9-12.

Received: 01. 02. 2018.

Accepted: 07. 04. 2018.