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INFLUENCE OF SYNTHESIS ON COMPOSITE/LAMINATED STARCH-GELATINE BASED BIOPOLYMER FILM PROPERTIES

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ABSTRACT

Biopolymer films have an increasing share in the packaging material sector due to a number of advantages: availability, cheapness, easy processing, degradability, etc. On the other hand, numerous methods have been developed to optimize their unfavorable properties (weaker mechanical characteristics, hydrophilicity, etc.). This paper examines the influence of the synthesis method on starch-gelatin films properties. The starch-gelatin film was synthesized in a ratio 1:1 as a composite film (C). The second sample was obtained by gelatin film lamination on starch film (L). Plain starch film was used as a control (0). Mechanical, structural and physico-chemical properties of importance for the application of packaging materials were tested on the obtained samples. All the obtained biopolymer films were transparent and easy to handle. FTIR spectroscopy identified all characteristic groups and bonds formed in composite and laminated films. The results showed a significant contribution of gelatin in the developed biopolymer films compared to the control sample. Gelatin incorporated as a film component or as a separate layer improved mechanical properties and water solubility. Slight differences were observed between composite and laminated films because the effect of the method of added gelatin is minimal compared to the sample without the addition of gelatin.

Keywords: biopolymer films, starch, gelatin, synthesis, properties

1. INTRODUCTION

The Polymer packaging materials are the most popular in the international packaging market for a variety of reasons: strength, flexibility, workability, the ability to combine with other materials and low cost. However, two issues connected to the use of polymers in the packaging sector have emerged in recent years: the synthesis of polymers from non-renewable sources, as well as the environmental impact of their excessive usage and disposal [1]. Petroleum-based plastics are not biodegradable or compostable, resulting in a massive amount of plastic waste around the planet [2]. The food packaging business is a major contributor to plastic waste creation. In this segment, it appears that an alternative to synthetic polymer should be found. Biodegradable materials have been the subject of extensive research for the past decades: the prospect of employing renewable raw materials and agro-industrial waste as an alternative to synthetic polymers is being explored. There has been an increase in demand for packaging materials that are biodegradable, offer less environmental risk, and are made from sustainable and renewable resources [3]. Biopolymers fall into three broad categories [4]:

- Biopolymers extracted from biomass (agricultural, animal processing, forest, or ocean wastes)
- Polymers synthesized using the bio-originated or bio-derived monomeric units via classical polymer synthesis routes (polylactic acid, bio-based polyethylene terephthalate, and biopolyolefins)
- Polymers produced by genetically modified microorganisms (bacterial cellulose and polyhydroxyalkanoates).

The first group of biopolymers has received a lot of attention [5]. Biopolymer film is a free-standing sheet that can be deposited on or between food components, usually categorized according to the dominant building material. Polysaccharides (cellulose, chitin, pectin, starch, etc.), proteins (whey protein, casein, collagen, zein, soy protein, myofibrillar proteins of animal muscle), and lipids (free fatty acids, wax, paraffin, resin) derived from plants, marine, and domestic animals are the three main groups of biopolymer films sources [6,7]. Biopolymers must meet specific characteristics, regardless of their application,

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including good barrier properties (water, gas, and oil), mechanical properties (resistance, stress-resistance, flexibility), and aesthetic properties (translucence, lack of color) [8]. Because starch and gelatin are abundant, cheap, and biodegradable materials that are also edible and hence suitable for food contact [9], they have been extensively explored for the aim of designing packaging materials. Starch is one of the most widespread polysaccharides in nature, obtained from renewable sources, whose price is low, so the use of edible starch-based packaging in the field of food packaging is a potential direction for the development of packaging materials today. From starch, it is possible to easily form packaging films with good sensory properties (color, smell, taste), which do not adversely affect the packaged contents. Gelatin is a multipurpose substance utilized as a gelling agent, a stabilizer, a thickening, an emulsifier, and even as a microencapsulating agent in the culinary, pharmaceutical and cosmetic industries [10]. Because of its good film-formation capabilities and abundance in nature, it is one of the biomaterials of interest for the production of biodegradable films [11]. Gelatin–starch blends are also gaining popularity, as both are renewable resources with good film-forming qualities, resulting in films with unique attributes such as biodegradability and non-toxicity [12].
The aim of this paper was to produce starch-gelatin films by lamination and by making composite film. Further, the aim was to characterize the properties of synthesized biopolymer films based on starch and gelatin obtained by lamination of one layer of biopolymer on another (L) and composite films obtained by mixing filmogenic solutions (C). Starch film was used as a control (0) in order to compare obtained results and propose more suitable film preparation method.

2. MATERIALS AND METHODS

2.1. Materials

Modified corn starch (C*EmTex 12688), was provided by Palco (Serbia), while gelatin was procured from Barentz (Serbia). Glycerol (99,8%) was purchased from Laboratorija (Serbia).

2.2. Methods

Starch solution preparation: Aqueous modified corn starch solution (1.5 % (w/v)) was heated at 90 ˚C in a water bath for 60 min with the addition of glycerol (40% of the starch mass).
Gelatin solution preparation: Aqueous gelatin solution (7% (w/w)) was prepared and left for 30 minutes at room temperature to undergo gelation, and then dissolved in a water bath at 50°C for about 20 min. Afterwards, 0.2 g glycerol/g gelatin was added and stirred.
Control sample (0) preparation: 50 g of starch solution was poured on Petri dishes coated with Teflon and left to dry for 5 days at room temperature on a leveled area after which they were analyzed.
Laminated sample (L) preparation: after pouring 40 g of starch film solution in Petri dishes coated with Teflon, they were left to dry. After 5 days 20g of gelatin solution was poured on their surface and left to dry on leveled surface after which they were analyzed.
Composite film (C) preparation: after preparing starch film solution and gelatin film solution, both solutions were mixed in a ratio 1:1. Obtained solution was poured in Petri dishes coated with Teflon (50g) and left to dry for 5 days at room temperature on a leveled area after which they were analyzed.

2.3. Mechanical properties

Film thickness was surveyed with 1 μm sensitivity micrometer. Eight replicates were carried out on each sample.
Tensile strength (TS) and elongation to break (EB) were evaluated by utilizing Instron Universal Testing Instrument Model No 4301 (Instron Engineering, Canton, Massachusetts, USA), in accordance with EN ISO 527-3:2018. The grip separation was set at 50 mm, and crosshead speed was 50 mm/min.

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2.4. Physical properties

Moisture content was determined as a percentage of weight reduction during film drying, expressed on the total weight of the film:

$$MC\ (\%) = 100\ [(m2-m1) - (m3-m1)]/\ (m2-m1) \quad (1)$$

where: m1- mass of measuring vessel, m2- mass of film samples with measuring vessel prior drying, m3- mass of dried film samples with measuring vessel

Swelling capacity: Film samples (2x2 cm) were weighed (m1), and then dipped in 20 ml of deionized water at room temperature, for 2 min. After removing samples from the water, the excess water was removed by a filter paper and samples were reweighed (m2). Swelling degree was calculated:

$$Swelling\ (\%) = 100\ (m2 - m1) / m1 \quad (2)$$

where m1- mass of film samples prior to dipping in deionized water, m2- mass of film samples after dipping in deionized water

The film solubility: Dry film samples, after moisture content determination, were submerged in 20 ml of deionized water at room temperature for 30 min, with mixing. After 30 min, excess water was emptied and samples were dried in the oven, for 60 min, and reweighed (m4). The solubility was calculated:

$$Solubility\ (\%) = 100\ [(m3–m1) - (m4-m1)]/\ (m3–m1) \quad (3)$$

where, m1- mass of measuring vessel, m2- mass of film samples with measuring vessel prior drying, m3- mass of dried film samples with measuring vessel, m4- mass of dried film samples with measuring vessel after immersion and drying

2.5. Structural properties

Fourier transform spectroscopy (FTIR) analysis of the film samples was carried out using the IR spectrophotometer, Nicolet IS10, Thermo Scientific (Massachusetts, USA). Omnic 8.1. software was used to operate the FTIR spectrometer, collect and process all the data.

2.6. Statistical analysis

MicroSoft Excel was used to run statistical analysis for calculating the means and standard error (MicroSoft Office 2010).

3. RESULTS

Results related to mechanical properties are presented in Table 1.

Table 1. Mechanical properties of control film, laminated and composite film

Sample	Thickness (μm)	Tensile strength (N/15mm)	Elongation at break (%)
Control	100.11±5.00	13.94±1.24	30.88±7.58
Laminated film	163.67±6.30	102.72±17.12	2.06±0.70
Composite film	211.00±5.96	75.92±12.66	1.33±0.16

According to the obtained results it was concluded that gelatin addition improved mechanical properties. Tensile strength increased while elongation at break values decreased. The highest tensile strength was at laminated samples, which were the firmest, no matter composite film had highest thickness value.

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Results related to physical properties are presented in Table 2.

Table 2. Physical properties of control film, laminated and composite film

Sample	Moisture content (%)	Swelling (%)	Solubility (%)
Control	18.17±0.05	234.12±29.41	73.68±3.78
Laminated film	11.41±1.02	109.35±5.16	22.12±1.61
Composite film	12.36±0.44	127.62±11.17	20.76±0.98

The gelatin addition improved swelling and solubility, which are considered undesirable characteristics of packaging materials, since values were lower compared to control film. There was no difference regarding film synthesis route- - weather it was laminated or composite.

Results obtained via FTIR are presented at Figure 1.

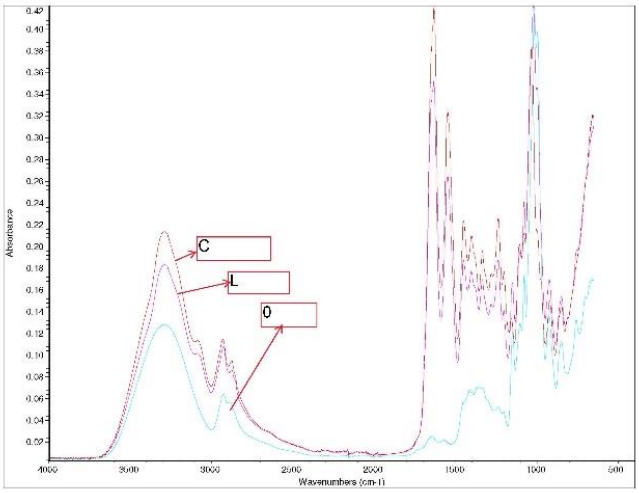

Figure 1. Control film, laminated and composite film spectra

Presence of absorption band at 3300-3600, 2900, 1640 and 1000-1100 cm-1 indicated that all samples contain starch with OH, C-H, C-O-C, and C-O functional group, respectively. C and L spectra contain both starch and gelatin and show almost similar peaks related to gelatin presence: four major peaks at wavenumbers 3500- 2300 cm-1, 1656-1644 cm-1, 1560-1335 cm-1 and 1240-670 cm-1 which correspond to Amide A, Amide I, Amide II, and Amide III regions, respectively.

4. DISCUSSION

When compared to their synthetic counterparts, biopolymers have inferior barrier, thermal, and mechanical qualities [13]. Polymer blending is a well-known method for developing new materials and optimizing polymer characteristics, resulting in composite polymers with superior properties to those generated from pure components [14]. The addition of hydrocolloids to the starch protects the granules from shearing during the manufacturing process. They retain moisture and diminish the blend's syneresis, water solubility, and water absorption [15]. The addition of starch to gelatin films increases the thickness, transparency, and mechanical strength of the films, decreases their solubility, and enhances their structure, all of which increase the films' application [16]. Various results were reported regarding starch-gelatin

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biopolymer films properties. According to the results of Silva et al. [17] the inclusion of gelatin increased films' mechanical strength and water solubility. On the other hand, according to results of Al-Hassan and Norziah [18] gelatin addition to starch films reduced tensile strength and water vapor permeability but increased the percentage of elongation at break. The same study proved interaction between polysaccharides and proteins, clearly visible using FTIR.
The obtained results in this study are in accordance with Fakhouri et al. [19] findings: gelatin incorporation improves water solubility, thickness, mechanical strength and clarity of starch-based films due to hydrogen bond formation between gelatin and starch as shown by Fourier transform infrared (FTIR) spectroscopy [16]. Fakhoury et al. [19] also found that higher gelatin concentrations increased water solubility, thickness and mechanical strength values, and reduce opacity. However, higher concentrations of starch increased the thickness and improve the mechanical properties. Gelatin incorporation resulted in tougher films with improved break resistance which was sustained with previous finding of Acosta et al. [20].

4. CONCLUSION

The goal of this paper was to evaluate the properties of biopolymer films based on starch and gelatin that were made by laminating one layer of biopolymer on top of another (L) and composite films made by mixing filmogenic solutions (C). In order to compare the results and suggest a better film preparation procedure, starch film was utilized as a control (0). The obtained results of this paper are in favor of the fact that starch films are improved by the addition of gelatin. The method of film preparation (lamination/composite films) did not affect the monitored physical characteristics of the films. The most pronounced differences between laminated and composite have been observed by monitoring the mechanical characteristics so the lamination is suggested as the optimal method of film preparation.

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REFERENCES

[1] T. Schwarzbock, E. Van Eygen, H. Rechberger, J. Fellner, Determining the amount of waste plastics in the feed of Austrian waste-to-energy facilities, Waste Management & Research, 35 (2016), pp. 207–216. https://doi.org/10.1177/0734242X16660372.
[2] A., Moeini, N., Germann, M., Malinconico, G., Santagata, Formulation of secondary compounds as additives of biopolymer-based food packaging: A review, Trends in Food Science & Technology, 114 (2021), pp. 342-354. https://doi.org/10.1016/j.tifs.2021.05.040.
[3] Y. Han, M., Yu, L., Wang, Physical and antimicrobial properties of sodium alginate/carboxymethyl cellulose films incorporated with cinnamon essential oil, Food Packaging and Shelf Life, 15 (2018), pp. 35–42. https://doi.org/10.1016/j.fpsl.2017.11.001.
[4] M.J., Fabra, A., López-Rubio, J.N., Lagaron, Biopolymers for food packaging applications. In: Smart Polymers and their Application. Elsevier, 2014, pp. 476–509. https://doi.org/10.1533/9780857097026.2.476.
[5] S., Popović, V., Lazić, N., Hromiš, D., Šuput, S., Bulut, Biopolymer packaging materials for food shelf-life prolongation. In: Biopolymers for food design, Academic Press, Elsevier, 2018, pp. 223-277 https://doi.org/10.1016/B978-0-12-811449-0.00008-6.
[6] D., Šuput, V., Lazić, S., Popović, N., Hromiš, Edible films and coatings – sources, properties and application, Food and Feed Research, 42 (2015), pp.11-22. https://doi.org/10.5937/FFR1501011S.

[7] D., Šuput, D. Sinteza, karakterizacija, optimizacija svojstava i primena jestivog, aktivnog ambalažnog materijala na bazi skroba. PhD Thesis, University of Novi Sad, Faculty of Technology Novi Sad, 2016.
[8] D. Kowalczyk M., Kordowska-Wiater J., Nowak, B., Baraniak, Characterization of films based on chitosan lactate and its blends with oxidized starch and gelatin, International Journal of Biological Macromolecules, 77 (2015), pp. 350–359. https://doi.org/10.1016/j.ijbiomac.2015.03.032.
[9] P., Cazón, G., Velazquez, J.A., Ramírez, M., Vázquez, Polysaccharide-based films and coatings for food packaging: A review, Food Hydrocolloids, 68 (2017), pp. 136–148. https://doi.org/10.1016/j.foodhyd.2016.09.009.
[10] L., Lin, J.M., Regenstein, S., Lv, J., Lu, S., Jiang, An overview of gelatin derived from aquatic animals: properties and modification, Trends in Food Science and Technology, 68 (2017), pp.102–112. https://doi.org/10.1016/j.tifs.2017.08.012
[11] N., Suderman, M.I.N., Isa, N.M., Sarbon, The effect of plasticizers on the functional properties of biodegradable gelatin-based film: a review, Food Bioscience, 24 (2018), pp. 111–119. https://doi.org/10.1016/j.fbio.2018.06.006.
[12] C. Shi, F., Tao, Y., Cui, New starch ester/gelatin-based films: developed and physicochemical characterization, International Journal of Biological Macromolecules, 109 (2018), pp. 863–887. https://doi.org/10.1016/j.ijbiomac.2017.11.073 .
[13] N., Jabeen, I., Majid, G.A., Nayik, Bioplastics and food packaging: A review, Cogent Food & Agriculture, 1 (2015), pp. 1117749. https://doi.org/10.1080/23311932.2015.1117749.
[14] B.A.L., Perez, E., Agama-Acevedo, E. Starch. In Starch-Based Materials in Food Packaging. Elsevier, (2017), pp. 1–18. https://doi.org/10.1016/b978-0-12-809439-6.00001-7.
[15] K., Mahmood, H., Kamilah, P.L., Shang, S., Sulaiman, F., Ariffin, A.K., Alias, A review: interaction of starch/non-starch hydrocolloid blending and the recent food applications, Food Bioscience, 19 (2017), pp.110–120. https://doi.org/10.1016/j.fbio.2017.05.006.
[16] K., Wang, W., Wang, R., Ye, J., Xiao, Y., Liu, J., Ding, J., et al., Mechanical and barrier properties of maize starch - gelatin composite films: Effects of amylose content, Journal of the Science of Food and Agriculture, 97 (2017), pp.3613–3622. https://doi.org/10.1002/jsfa.8220.
[17] N.M., Silva, F.M., Fakhouri R.L.L., Fialho, E.C.D.M.A., Albuquerque, Starch-recycled gelatin composite films produced by extrusion: physical and mechanical properties, Journal of Applied Polymer Science, 135 (2018), pp.46254. https://doi.org/10.1002/app.46254.
[18] A.A., Al-Hassan, M.H., Norziah, Effect of transglutaminase induced crosslinking on the properties of starch/gelatin films, Food Packaging and Shelf Life, 13 (2017), pp.15–19. https://doi.org/10.1016/j.fpsl.2017.04.006.
[19] F.M., Fakhoury, S.M., Martelli, L.C., Bertan, F., Yamashita, L.H.I., Mei, F.P.C., Queiroz, Edible films made from blends of manioc starch and gelatin – influence of different types of plasticizer and different levels of macromolecules on their properties, LWT 49 (2012), pp.149–154. https://doi.org/10.1016/j.lwt.2012.04.017.
[20] S., Acosta, A., Jiménez, M., Cháfer, C., González-Martínez, A., Chiralt, Physical properties and stability of starch–gelatin-based films as affected by the addition of esters of fatty acids, Food Hydrocolloids, 49 (2015), pp. 135–143. https://doi.org/10.1016/j.foodhyd.2015.03.015.

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