

DEVELOPMENT OF BIODEGRADABLE PACKAGING FILMS AND EDIBLE COATINGS FOR FOOD PRODUCTS BASED ON COMPOSITE MATERIALS

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Abstract

Plastic is undoubtedly the most convenient type of packaging, but at the same time it is not ecologically friendly. The widespread use of packaging materials all over the world makes us think more and more about the harm of plastic to the environment and humans. It does not decompose in natural conditions and accumulates in huge quantities, because it is mostly used as a single-use packaging. Therefore, the development of environmentally friendly biodegradable edible films and coatings is relevant. Edible food packaging is an important step in food production and one of the innovative directions of food packaging development. This article presents materials on the development of the formulation and manufacturing technology of new composite materials based on sodium alginate and chitosan for the production of edible coatings and films. The results of the physical, chemical and bactericidal properties of these materials are presented.

Key words: *chitosan, biodegradable food films and coatings, edible films and coatings, environmental protection, sodium alginate, physicochemical, bactericidal properties*

Received: 17.03.2020

Accepted: 28.05.2020

1. Introduction

The problem of recycling synthetic polymer packaging materials is very acute [1]. Every year, about 8 million tons of non-biodegradable wastes are discharged into the ocean. In soil, the period of assimilation of synthetic polymers is tens or even hundreds of years.

Directive 94/62/EC [2] on the reduction in the use of light (thickness <50 µm) and ultralight (<15 µm) plastic bags, approved by the European Parliament in 2015, states that the annual consumption of light bags per capita should not exceed 40 pieces by 31 December 2025. The Directive also notes that oxo-biodegradable and oxo-degradable plastic bags are essentially not biodegradable, because hydroxy additives only contribute to the destruction of plastic to small particles that are not biodegradable and remain in the environment for a long time.

In this regard, one of the urgent areas of research is the development of environmentally friendly biodegradable edible films and coatings. Edible food packaging is an important step in food production and one of the innovative directions in the development of food packaging. The main difference between edible films and coatings from traditional biodegradable plastics is that they are the only type of biodegradable polymer packaging that does not need to be selected from other waste and special disposal conditions [3]. Edible films and coatings, as well as synthetic ones, must protect the product from mechanical damage, physical and chemical factors as well as microbiological damage. Their use in the food industry is governed by the presence of a number of indicators: satisfactory mechanical properties (flexibility, stretching, tensile strength); optical properties (transparency, tarnish); vapour, gas and aroma permeability; light, heat and frost resistance; structural resistance to exposure to microorganisms; as well as organoleptic indicators.

According to their nutritional value, edible films and coatings are subdivided into assimilable ones, which are obtained on the basis of proteins, fats, carbohydrates and non-assimilable (natural waxes, water-soluble natural and synthetic gums, water-soluble derivatives of cellulose, polyvinyl alcohol, polyvinylpyrrolidone, etc.) and are neither absorbed by nor removed from the human body [4]. Non-assimilable coatings have an allowable daily safe intake in the human body throughout life.

The number of investigations devoted to edible films – as well as their use – has been limited. This is mainly due to their unsatisfactory physicochemical and/or sensory properties. The main requirements for edible packaging are its non-toxicity, as well as environmental and sanitary safety. Of particular interest is packaging that does not contain preservatives but does have antimicrobial properties.

Chitosan-biodegradable polymer with enhanced antimicrobial and sorption properties, as well as the necessary rheological characteristics, has been considered for manufacturing solutions used as films and coatings [5]. Its sorption properties provide the ability to remove previously accumulated toxic heavy metals and radionuclides from the body, an action that cleanses the body of toxins and wastes. Chitosan is noncaloric and forms stable gels capable of selectively binding molecules of ‘harmful fats’ – triglycerides and cholesterol, an action that contributes to weight loss – without absorbing unsaturated fatty acids [6]. Chitosan forms sufficiently strong, albeit inelastic, films.

Both sodium alginate and chitosan polysaccharide polymer have a cellular structure, which explains their ability to form stable thermostable gels. Alginate effectively removes radionuclides and heavy metals from the body, has antacid properties, lowers blood cholesterol, forms part of weight loss products and many dietary supplements and is harmless to humans [7]. Alginate, like chitosan, is noncaloric. The undoubted advantage of alginates is their ability to cure and form form-stable elastic hydrogels under the action of divalent metal ions.

A common drawback of gel polymers is the duration of the gel drying process at high temperatures, which makes them inappropriate to use as coatings for food products (meat, fish, etc.). Hence, it is advisable to develop an edible coating, based on sodium alginate and chitosan, which would combine the advantages of each of them, namely: the ability to quickly form an alginate film (curing), biocidal properties, the ability of chitosan to selectively absorb harmful fats, the ability to eco-rehabilitation of the body from toxins, low calorie content and biodegradability of both polymers. In this case, it is possible to expect an improvement in the physico-mechanical properties of the new coating due to the strength of the chitosan films and the elasticity of the alginate gels.

In the past, the development of a composite material based on polymers of sodium alginate and chitosan in one coating had been impossible because of their thermodynamic incompatibility. As is commonly known, when drying, they are stratified into two phases and there is loss of physical and mechanical characteristics of the coatings. However, there are approaches for treating thermodynamically incompatible polymers with surfactants and plasticizers; these techniques provide the possibility of their joint use in composite materials [8]. The aim of the work was to develop the formulation and manufacturing technology of new composite materials based on sodium alginate and chitosan – to obtain edible coatings and films – to develop a technology for applying them to products to study the physicochemical properties of these materials.

2. Materials and Methods

2.1. Materials

This study utilized the following materials:

- High-molecular chitosan from the shell of crustaceans (physicochemical properties are given in Table 1). This product was supplied by the limited liability company 'Bioprogress'. It is a light cream-coloured powder;
- Sodium alginate from Japanese kelp algae (physicochemical properties are given in Table 1);
- The surfactant E472 is an ester of sorbitol hexahydrate and stearic acid that has been approved for use in the food industry;
- Citric acid (p.a.), a white crystalline powder;
- Distilled water; and
- Calcium chloride (p.a.), a white granule.

Table 1. Physicochemical properties of sodium alginate and chitosan.

Polymer	Sodium alginate	Chitosan
Solubility in 2% acetic acid, %	100.0	99.7
Solubility in water, %	100.0	insoluble
Humidity, %	13.5	10.0
Ash content, %	17.38	0.46
Amine nitrogen, %	–	8.48
-COOH, %	17.60	–
Degree of deacetylation, %	–	98.0
Kinematic viscosity of a 2% solution, cPs	13.98	3173.6
Molecular mass, kDa	63.0	224.5

2.2. Analytical Methods

Amine nitrogen was determined by the formal titration method. The method is based on the interaction of amino acids with formalin, resulting in the formation of methylene compounds, acids, which are titrated with alkali. The content of amine groups is calculated according to the amount of alkali spent on titration, [9].

The chitosan degree of deacetylation was determined by potentiometric titration [10] of its solutions in a hydrochloric acid solution (0.1 N) with a potassium hydroxide solution (0.1 N) using an Ecotest 2000 ion meter.

The molecular weight of chitosan was determined in 1L of a solution containing 0.3 M sodium chloride and 0.33 M acetic acid. The molecular weight of sodium alginate was determined in a solution with 0.1 M sodium chloride [11].

The content of functional groups in polymers was determined according to previous procedures [11, 12] by the potentiometric method on an ANION 4100 ionometer with a glass combined electrode ($\Delta = 0.05$ pH, $T = 23^\circ\text{C}$). The content of free carboxyl groups (Kc,%) in sodium alginate was calculated by Eq.1:

$$Kc = \frac{C_{NaOH} \cdot V_{NaOH} \cdot 45}{V_{alg} \cdot 1000} \cdot \frac{V_{bottle}}{V_{alg}} \cdot 100\%, \quad (1)$$

where m_{alg} is the weighed amount of polysaccharide [g], 45 is the alkali equivalence coefficient for carboxyl groups and V_{NaOH} is the volume of alkali used for titration (in mL).

2.3. Film Preparation

The prepared film-forming solution was applied to the prepared surface and combined with a calcium chloride solution to enable the film-forming process. The thickness of the finished film depended on the amount of the prepared mixture. The film-forming composition was applied to an even, clean horizontal surface and left for 24 h to complete the process. To make films, a film-forming solution was poured into Petri dishes with a diameter of 89 mm. Drying was carried out in a BinderED-115 thermostat at 50°C for 24 h.

2.4 Film Thickness Measurement

To measure the film thickness, a MK 50-1 micrometer and the direct measurement method were used. Ten parallel measurements in three different sections of the film were carried out and the average value was determined.

2.5 Determining Bactericidal Properties

Bactericidal properties were studied using cultures of *Staphylococcus aureus* ATCC 25923 and *Escherichia coli* ATCC 25922. Microorganisms were streaked on dense Givental-Vedmin nutrient agar medium, which is a mixture of dry components in the form of a finely divided, hygroscopic yellow powder, to generate a 'lawn'. The composition of the nutrient medium (g/L) was: pancreatic hydrolyzate of fish meal, 21.0; enzymatic peptone, 10.0, starch, 1.5; sodium chloride, 3.0; and microbiological agar, 12.0 ± 3.0 .

A 4-mm diameter film was placed on a bacterial lawn culture and incubated for 24 h. The diameter of the inhibition zone around the test film sample was used to evaluate bacterial activity. The results were obtained by averaging five parallel samples.

2.6 Determining the Degree of Water Absorption

Rectangular film samples (3×2 cm) were dried in a thermostat (50°C) during the day, then cooled in a desiccator to 23°C and weighed (W_1). Then, each sample was placed in a test tube (50 mL) containing 10 mL of distilled water. Samples were stored for 24 h

at room temperature and periodically slowly mixed, after which the solution was filtered, and the precipitate on filter paper was dried in the thermostat at 105°C for 24 h, after which the samples were weighed and the amount of dry matter was determined (W_2).

Solubility was calculated by Eq. 2:

$$P = \frac{W_1 - W_2}{W_1} \cdot 100\%, \quad (2)$$

where P is the solubility (%), W_1 is the mass of the sample dried in a thermostat before filtering and W_2 is the mass of the sample dried in a thermostat after filtration.

2.7 Determining Physical and Mechanical Properties

Strength (St) and elongation in tension (L) were measured on the Instron 3343 electromechanical testing machine using 35 × 50 mm samples. The maximum force required to tear each film was read from the digital display of the device. Strength was calculated by dividing the maximum tensile strength (F) by the cross-sectional area of the film sample (S), which was obtained by multiplying the width by the average thickness of the film strips. Strength was calculated using Eq. 3:

$$St = \frac{F}{S}, \quad (3)$$

where F is the maximum strength of the break and S is the cross-sectional area of the film sample.

The elongation in tension (L) was calculated by dividing the increase in the length of the film strips at break (b) by the initial length of the film strips before loading (a), according to Eq. 4:

$$L = \frac{b}{a} \cdot 100\%. \quad (4)$$

3. Results and Discussion

Solutions of chitosan, surfactant E472, sodium alginate and also liquid vegetable oil were used to manufacture biodegradable film samples. Chitosan was used as a 2%–3% solution in 3%–5% citric acid. The amount of insoluble precipitate was not more than 1.0%. Chitosan citrate was mixed with an aqueous mixture of 3–7% surfactant and vegetable oil mixed with a blender for 2 minutes. Next, a 1%–3% aqueous solution of sodium alginate was added and mixed with a blender. Thus, a film-forming mixture was obtained, which was applied to the prepared substrate, then cured with a 2%–5% solution of calcium chloride for 60 min at 20°C (Fig. 1).

A search was carried out for optimal concentrations of the components of the composite material (Table 2). Citric acid was chosen as the solvent for chitosan considering that it is used in the food industry. Vegetable oil in the mixture is used as the filler (plasticizer) in the layers (fibres) of high-molecular-weight chains forming the framework of the polymer (film) being created. Vegetable oil, as a substance approved for use in the food industry, helps to improve the physical and mechanical properties of the film, increasing the elasticity of the polymer and resistance to repeatedly bending without cracking.

The composition of the film-forming composition is indicated in the form of intervals (Table 2), because depending on the film's required properties, for example, greater elasticity or greater strength, the number of components may vary. However, they would not go beyond the indicated intervals.

The organoleptic properties of the film corresponded to the properties of the packaging materials. The film surface was smooth, without cracks; the texture was dense, without the inclusion of undissolved and foreign particles; the colour was matte white; and it was



Figure 1. Chitosan-alginate film-forming mixture.

Table 2. The composition of the film-forming mixture.

Material	Quantity,%
Chitosan solution in citric acid	6–10
Vegetable oil	18–23
Surfactant solution E472	11.2–15.6
Sodium alginate solution	53–76
Calcium chloride solution	unlimited

Table 3. Bactericidal properties of four-component chitosan-alginate films.

Chitosan concentration,%	Growth inhibition zone diameter, mm	
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>
0.090	8.1±0.4	7.2±0.4
0.135	8.6±0.3	7.9±0.7
0.160	9.2±0.5	11.3±0.5
0.200	11.0±0.3	12.6±1.0
0.240	11.0±0.4	12.4±2.0

tasteless, odourless and presented good chewiness. As a result of mixing, air bubbles were formed, which were removed by vacuuming the film-forming mixture before solidification. The biodegradable film made by this method with the introduction of chitosan into the mixture was 0.19–1.20 mm thick.

The bactericidal and sensory properties of the four-component chitosan-alginate films, depending on the concentration of chitosan, are presented in Table 3. The bactericidal properties were better in films where the chitosan content is at least 0.2%.

To study the influence of the thickness of the developed film materials on their consumer properties, their strength and elastic characteristics were determined (Table 4). The obtained biodegradable packaging material had satisfactory quality characteristics and thus could be used as a coating applied directly to the product. As a test experiment, the developed chitosan-alginate composition was applied to chilled 6 cm³ pieces of cod and catfish. Fig. 2 shows product samples after immersion in a calcium chloride solution to cure the coating. The chitosan-alginate coating was not destroyed during heat treatment (cooking, frying) and prevented the loss of moisture in fish samples.

Table 4. Physico-mechanical characteristics of four-component chitosan-alginate films of different thicknesses.

Chitosan concentration, %	Alginate concentration, %	Film dimensions, mm	Average thickness, mm	Tensile strength, MPa	Relative extension, %
0.2	1.5	35 × 50	1.18	32	155
		35 × 50	1.16	55	135
		35 × 50	1.14	41	139

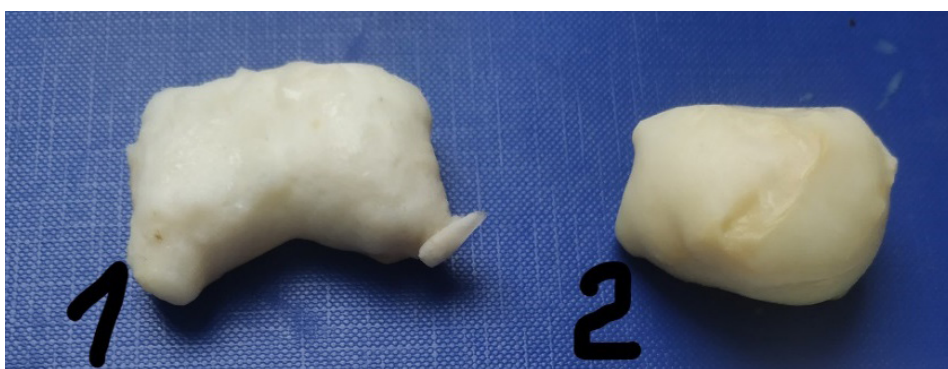


Figure 2. Samples of cod (1) and catfish (2) pieces with chitosan-alginate film applied to them.

4. Conclusions

This work developed technology for combining sodium alginate and chitosan in one composite material to produce biodegradable food packaging films with satisfactory physicochemical and bactericidal properties. The biodegradable film can be applied to the surface of moulded minced products (e.g. sausages, meatballs) and meat and fish fillets.

Moulded products or fillets are wetted with a prepared film-forming composition, which is instantly fixed when introduced into the hardener (calcium chloride solution) at room temperature. The biodegradable film protects the surface of food products from the effects of harmful factors, prolongs the shelf life and can be used in a food product, because it has the properties of biologically active additives. It is frost and heat resistant. The film combines the advantages of chitosan and sodium alginate, namely, along with bactericidal activity, it has a low calorie content, the ability to eco-rehabilitate the human body by sorption and excretion of harmful impurities and improves intestinal function, among others.

5. References

- [1] Wróblewska-Krepsztul, J., Rydzkowski, T., Borowski, G., Szczypiński, M., Klepka, T., & Thakur, V. K. (2018). Recent progress in biodegradable polymers and nanocomposite-based packaging materials for sustainable environment. *International Journal of Polymer Analysis and Characterization*, 23(4), 383-395.
- [2] Directive 94/62/ EC as regards reducing the consumption of lightweight plastic carrier bags // Directive (EU) 2015/ 720 of the European Parliament and of the council [Electronic resource]. – 2015. – Mode of access: <http://eur-lex.europa.eu/legalcontent/EN/TXT/?uri=CELEX:32015L0720>. – Date of access: 03.03.2016.
- [3] Savitskaya, T. A. (2016). Edible polymer films and coatings: background and current state (review). *Polymer materials and technologies*, 2(2), 6.
- [4] Kasyanov, G. I. (2015). The bio-decomposable packaging for food products. *Bulletin of science and education of the North-West of Russia*, 1(1).
- [5] Kuprina, E. E., Kiprushkina, E. I., Shestopalova, I. A., Yakkola, A. N., Manuylov, A. N., Odegova, N. V., ... & Mushits, A. I. (2018). Research of the influence of chitin-containing food additives on the rheological properties and biological value of minced fish. *Progress on Chemistry and Application of Chitin and its Derivatives*, 23, 114-119.
- [6] Kuprina, E. E., Kirillov, A. I., Ishevski, A. L., & Murashev, S. V. (2015). Food supplement based on chitin with enhanced lipid-lowering and sorption properties. *Progress on Chemistry and Application of Chitin and its Derivatives*, 20, 156-161.
- [7] Mukatova, M. D., Skolkov, S. A., Moiseenko, M. S., & Kirichko, N. A. (2018). Food-grade biodegradable film using chitosan. *Bulletin of the Astrakhan state technical University. Series: fisheries*, (3).
- [8] Tager, A. A. (1978). *Physical chemistry of polymers*. Ripoll Classic.
- [9] Величко, Н. А., & Шанина, Е. В. (2010). *Пищевая химия*.
- [10] Bodek, K. H. (1994). Potentiometric method for determination of the degree of acetylation of chitosan. In "Chitin World" (Z. S. Karnicki, M. M. Breziski, P. J. Bykowsky, A. Wojtasz-Pajak, Eds.), pp. 456-461. *Wirtschaftsverlag NW-Verlag*, Germany.
- [11] Brovko, O. S., Palamarchuk, I. A., Val'chuk, N. A., Chukhchin, D. G., Bogolitsyn, K. G., & Boitsova, T. A. (2017). Gels of sodium alginate–chitosan interpolyelectrolyte complexes. *Russian Journal of Physical Chemistry A*, 91(8), 1580-1585.
- [12] Scriabin, K. G., Mikhailov, S. N. Varlamov, V. P. (2013). *Chitosan*.