PREPARATION AND REGULATION OF STRUCTURAL-MECHANICAL PROPERTIES OF BIODEGRADABLE FILMS BASED ON STARCH AND AGAR

The problem of recycling polymer waste is one of the most actual problems. One way to solve this problem is to create biodegradable food packaging. By mixing solutions of starch and agar at different mass ratios of polymers in the presence of glycerol, biodegradable films are obtained. Their structural and mechanical characteristics are determined. It is shown that the values of strength, modulus of elasticity and puncture resistance of films are maximal at the mass ratio of agar/starch 7-9. A comparison of the roughness of the films obtained from starch, agar and their mixture showed that the greatest roughness is possessed by films based on starch. The introduction of agar into the films of starch leads to a significant reduction in their roughness.

To regulate the structural and mechanical properties of films, it is proposed to use Ca and Mg salts. The influence of Ca^{2+} and Mg^{2+} ions on the strength and deformation characteristics of biofilms was studied. It is shown that Ca^{2+} ions monotonically increase the strength characteristics of starch-agar films, while the curves of changes in these parameters in the presence of Mg^{2+} ions have maxima at a concentration of 0.5 %. The difference in the effect of Ca^{2+} and Mg^{2+} ions on the structural and mechanical properties of films is explained by the hydration degree of these ions.

The biodegradability of starch-agar films was controlled by changing their IR spectra. The most significant changes are observed in the intensity and localization of peaks corresponding to O-H, C-H and C-C bonds, which can be evidence of changes in the structure of films due to the destruction of the grid of hydrogen bonds and hydrophobic interactions, as well as the break of hydrocarbon chains and the destruction of the skeleton of carbohydrate molecules

Keywords: biodegradable films, starch, agar, structure formation, mechanical properties, puncture resistance

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1. Introduction

Currently, the disposal of polymer waste is one of the most actual problems. If in the middle of the last century, the efforts of scientists and technologists were aimed at creating strong and stable polymer materials, now there is a problem of fighting the consequences of this task, that is, the decomposition of polymer packaging. Landfills of used polymer materials complement solid household waste, which are sources of water, air and soil pollution.

Among the polymer wastes that pollute the environment, the contribution of food packaging is very significant. These are plastic bags, bottles, disposable tableware, etc. The main part of the world's polymer materials is obtained from oil, gas and coal, whose reserves are not unlimited. The danger of uncontrolled use and accumulation of polymer waste in nature is that they are very strong and resistant to the effects of microorganisms and air oxygen. To solve the problem of cleaning the environment from them, various activities are carried out, such as separate garbage collection, recycling of polymer waste. However, the most effective way to solve this problem is to obtain polymers from renewable raw materials of plant or animal origin. Therefore, the creation of biodegradable food packaging that can be destroyed in natural conditions under the influence of moisture, temperature, light and microorganisms: bacteria, yeast and fungi is one of the priorities of science, industry and technology.

2. Literature review and problem statement

The main raw materials for producing biodegradable packaging films are polymers: gelatin, starch, carboxymethylcellulose, polyvinyl alcohol, etc. [1]. These polymers, in turn, can be divided into edible and inedible. Polysaccharides, proteins, and lipids are edible, while polyvinyl alcohol, polyangrides, and polylactic acid are inedible [2].

Most biodegradable films are composites consisting of two or more ingredients. Moreover, other polymers, fruit and vegetable pulp, plant extracts, various clays and salts can be used as additives to biopolymers [1–3], which give the films the specified properties. Based on 2 polysaccharides: carboxymethylcellulose and chitosan, double films were obtained that have protective properties when used as edible coatings for citrus fruits [3]. Gelatin, which has a complex amino acid composition, and, accordingly, various functional groups, is a potential raw material for producing such composites. To improve the physical and chemical properties of the resulting films, composites of gelatin with chitosan were obtained at different polymer ratios [4]. Indeed, the addition of chitosan caused a significant increase in tensile strength and elastic modulus, but reduced the elongation at break. However, in most cases, chitosan is injected into solutions of other biopolymers to give the films antimicrobial properties [5]. This is due to the fact that there are amine groups in chitosan macromolecules that give the polymer a positive charge and adversely affect the negatively charged functional groups of the bacterial cell membrane. To enhance the bactericidal properties of films, it is proposed to use chitosan modified with quaternary ammonium [6]. Films obtained on the basis of such modified chitosan and polyvinyl alcohol show high activity in inhibiting the growth of *Escherichia Coli, Staphilococcus aureus* and *Botrytis cinerea* bacteria. There are also examples of giving antimicrobial properties to food films using silver nanoparticles [7]. To do this, solutions of gelatin and silver nanoparticles were mixed using the solvent costing method. An increase in the concentration of silver nanoparticles led to a significant decrease in the water resistance and strength of gelatin films. The films showed high bactericidal activity against food-born pathogens.

An effective way to change the hydrophobicity of soy protein films was to introduce poly (lactic) acid into their composition [2], although it is a hydrophilic polymer. Obviously, the mutual attraction of oppositely charged functional groups of two polymers – protein amino groups and acid carboxyl groups – leads to the corresponding orientation of their hydrophobic groups, at which they turn outward.

The most significant characteristics of food films are strength and elasticity. The durability of the films depends on the properties of the initial material and the additives in composite material and the elasticity of films is usually adjusted with additives of glycerol [3, 8, 9]. The increase in the concentration of glycerol from 15 to 35 % in the films of exopolysaccharide, obtained from kefir grains, leads to higher extensibility, but reduces tensile strength due to an increase in mobility of polymer chains; this is a consequence of the plasticizing effect of glycerol [8]. In general, the addition of glycerol is justified by the formation of H-bonds between its molecules and the polymer, which can be considered as a soft destruction of the polymer matrix with an increase in chain mobility and a decrease in resistance to the applied stress [9]. Therefore, other substances capable of forming hydrogen bonds, such as sorbitol, are also used as plasticizers [10]. As for the protective properties in relation to food, the best were doubled films obtained by layer-by-layer [3].

Among the biopolymers used to produce food films, starch is the cheapest and most affordable. However, the films obtained from it are brittle, which makes it difficult to use them as packaging material [11]. In addition, it has low barrier indicators [12]. At the same time, to improve the properties of starch films, it is proposed to obtain its composites with other polymers [12, 13]. Indeed, the combination of starch with a synthetic polymer – polyvinyl alcohol (PVA) improves the properties of its films. In the case of [12], the introduction of PVA into the starch films caused an increase in their mechanical properties and gas permeability. In [13], the inclusion of PVA in the composition of cassava starch films led to the production of biodegradable films, but these films were stronger than polyethylene films. It can be assumed that mixing a starch solution with a solution of another polysaccharide – agar – will result in films with lower strength, which will increase their biodegradability. The choice of agar among other polysaccharides is due to the fact that the resulting films are likely to be used as edible coatings for food products in the future. Agar is widely used in the food industry and is part of most jelly products. Due to its ability to form a grid of hydrogen bonds, it has structure-forming properties. In addition, unlike other polysaccharides, its macromolecules retain water molecules for a long time.

3. The aim and objectives of the study

The aim of the study is regulation of structural-mechanical properties of films based on starch and agar.

To achieve this aim, the following objectives are accomplished:

– to obtain biodegradable films at different ratios of starch and agar;

– to determine the strength and deformation characteristics of starch-agar films;

– to study the influence of Ca^{2+} and Mg^{2+} ions on the structural-mechanical properties of starch-agar films.

4. Materials and method

4. 1. Object of research

As structure-forming agents, potato starch, STST 53876-2010 (Russia) and agar, TS (Technical specifications) 9398 – 020 – 7895326 – 2006 (Russia), were used in the work.

Calcium (STST 4460 – 66) and magnesium (TS 2152 – 002 – 93524115 – 2010) chlorides were used as Ca^{2+} and Mg^{2+} salts.

4. 2. Research methods
4. 2. 1. Obtaining of films

To obtain the films, 4 % solutions of starch and agar were prepared separately. The polymers were dissolved by stirring and heating up to 80 °C. Then the necessary amounts of each polymer were selected and their mixtures were prepared. The total volume of the mixture was 100 ml, and 2 g of glycerol was added to it. Mixtures of starch, agar and glycerol were stirred on a magnetic stirrer at 1,500 rpm/min for 10 minutes, then poured in glass cups and kept for 24 hours at 25 °C in a thermostat. The resulting films were separated from the surface of the cup, cut into samples measuring 15×4 cm and their elastic-strength characteristics were determined.

4. 2. 2. Method for determining the strength of films

To determine the structural and mechanical properties of biofilms, methods and devices to control the properties of oilcloth materials were used.

To determine the strength of the films, the film break mass was found on the MT-160 device (Russia) in accordance with STST 12088 – 77. The principle of operation of the device is based on the change in the tension force in the measuring

resistor sensor. The machine consists of two parts: the housing and the sensor. The desired conditions are set in the sensor, and the test sample is placed in the hole in the housing. The sample should be 15 cm long and 4 cm wide. After pressing the "Start" button, the values of the break mass in kilograms and elongation in millimeters appear on the screen.

Based on the results obtained with this device, it is possible to calculate the strength, deformation and elasticity of films [13].

$$\sigma = \frac{F}{S},$$

where σ – strength, [kPa]; F – the tear force of the film, [N]; S – film area, [m^2].

$$F = mg,$$

m – the mass of the gap, [g]; g – acceleration of gravity, [m/s^2].

$$\varepsilon = \frac{l}{\Delta l},$$

ε – deformation; l – the original length of the film, [mm], l – elongation, [mm].

$$E = \frac{\sigma}{\varepsilon},$$

E – modulus of elasticity, [kPa]; ε – deformation, σ – film strength, [kPa].

4. 2. 3. Measurement of puncture resistance

Puncture resistance of films was determined on the USPP – 2017 device according to STST 12.4.141 – 99 SSBT. The thickness of the films was determined on the MT – 531 device (Russia).

To determine the resistance to puncture, a sample was placed in a metal circle with a diameter of 20–25 mm and pierced with a needle with a diameter of 2.6 mm and a movement speed of 500 mm/min. The sensor displays the piercing force in kN. The unit retains its characteristics and can operate at temperatures from +10 °C to +35 °C and humidity up to 80 %.

4. 2. 4. Determination of film roughness

Changes in the surface roughness of films were studied by atomic force microscopy (AFM) using a scanning probe microscope (Integra Spectra), AFM – Raman – SBOM – TERS (Russia).

4. 2. 5. IR-spectroscopy

The IR spectra of the film tiles were taken using the "Avator 370 – CsI" Fourier IR spectrometer in KBr tablets. For research, starch-agar films were used, which were stored for 1 and 7 days.

5. Results

5. 1. Strength and deformation characteristics of starch-agar films

Fig. 1 shows the curves of dependence of the strength σ and modulus of elasticity ε of starch-agar films on the mass

ratio of agar/starch (m). The strength values are calculated based on the load mass required to break the film. To calculate the elastic modulus values, the relative elongation of the films was determined and their deformation was found. In the starch-agar mixture, an increase in the amount of agar leads to an increase in these characteristics. An increase in the m value from 0.7 to 9.0 leads to an increase in the strength values from 0.9 kPa to 2.8 kPa. A corresponding increase in the agar fraction is observed for the modulus of elasticity. It should be noted that with an increase in the amount of agar, along with the strength and elasticity, the film puncture resistance also increases (Fig. 2).
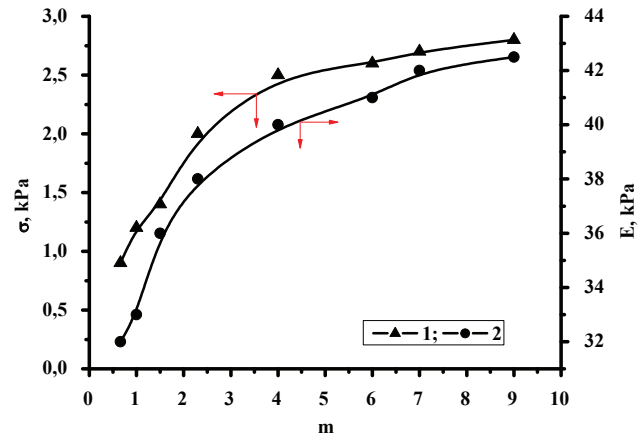

Fig. 1. Effect of agar/starch mass ratio on the strength and modulus of elasticity of films: 1 — strength; 2 — elasticity modulus
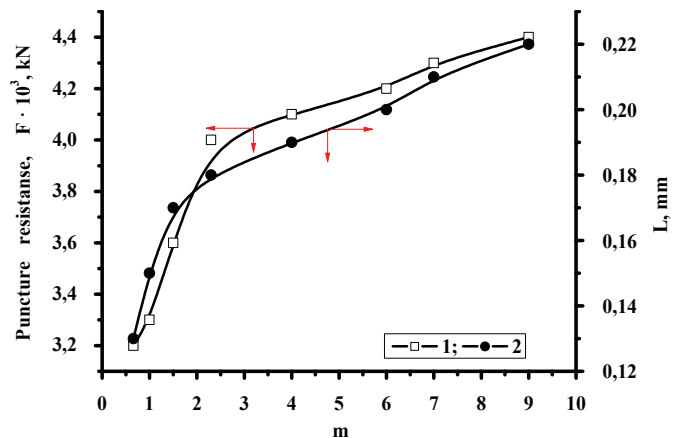

Fig. 2. Effect of agar/starch mass ratio on puncture resistance and thickness of films: 1 — puncture resistance; 2 — thickness

In general, in the area of changes in the mass ratio of agar/starch from 0.7 to 4.0, there is a sharp increase in all the studied structural and mechanical characteristics of the films: strength, modulus of elasticity and puncture resistance. With a further increase in the amount of agar in the films ($m \geq 4$), a monotonous increase in these characteristics occurs. Along with them, when the agar fraction increases, the thickness of the films increases.

5. 2. Roughness of the films

It should be noted that in the absence of starch, the agar solutions used are difficult to spread over the glass surface and do not form smooth films. Therefore,

it could be assumed that the addition of starch to agar solutions will lead to an increase in the uniformity of the films. However, the data on the roughness of the films (Fig. 3, *a–c*) show the opposite.
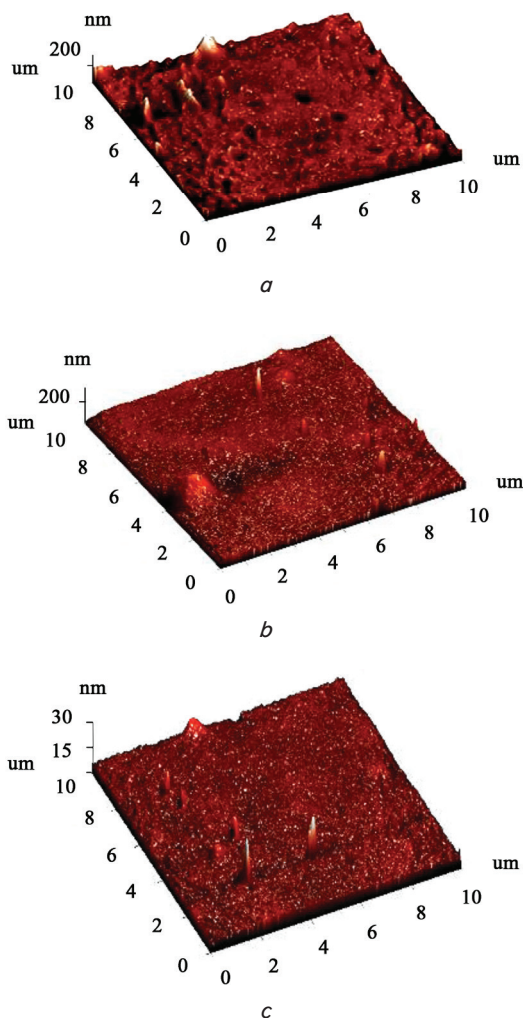

a

b

c

Fig. 3. Changes in film roughness in the systems: *a* – starch; *b* – agar; *c* – starch-agar at *m*=2.5

The roughness of the starch films was much higher than in the case of agar films, but mixing the two polymers leads to the formation of films approaching the roughness of the agar. The height of the peaks corresponding to the size of the polymer clumps that cause roughness is 200 nm for starch films, 20 nm for agar films, and 30 nm for the starch-agar system. Probably, the interaction of functional groups of two polysaccharides leads to solubilization of water-insoluble polymer clumps in their hydrophobic sites.

5. 3. Structural-mechanical characteristics of starch-agar films containing Ca^{2+} and Mg^{2+} ions

To regulate the structural and mechanical characteristics of films produced on the basis of starch and agar, Ca^{2+} and Mg^{2+} ions are introduced into their composition (Fig. 4–6).

It was found that the effect of Ca^{2+} and Mg^{2+} ions on the strength of films is different (Fig. 4). If the introduction of Ca^{2+} ions into the system leads to a monotonous

increase in strength values, then in the case of Mg^{2+} ions, the curve of strength dependence on the concentration of metal ions has a maximum at a salt concentration of 0.5 %.
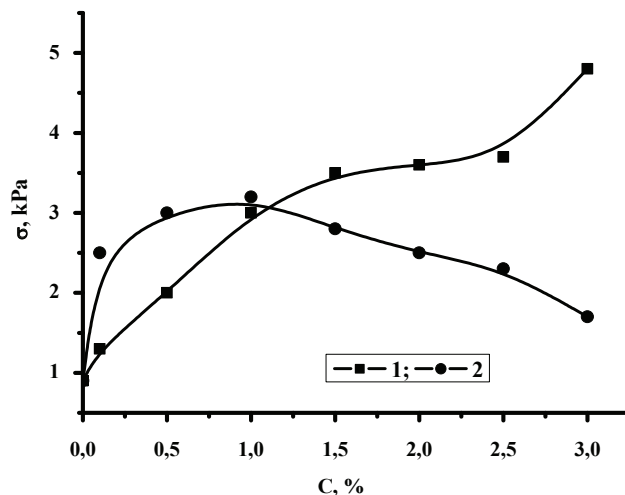

Fig. 4. Effect of metal ions on the strength of starch-agar biofilms at *m*=2.5: 1 – Ca^{2+}; 2 – Mg^{2+}
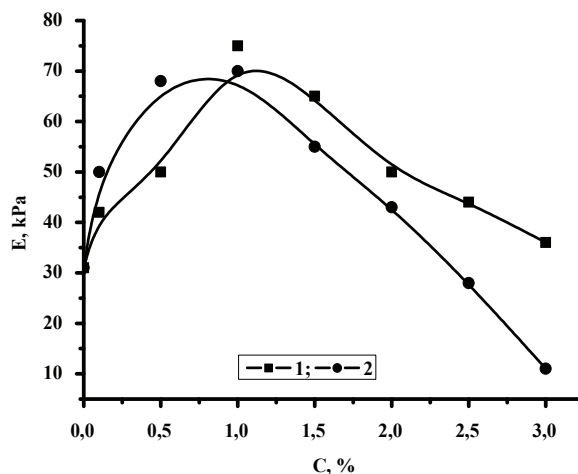

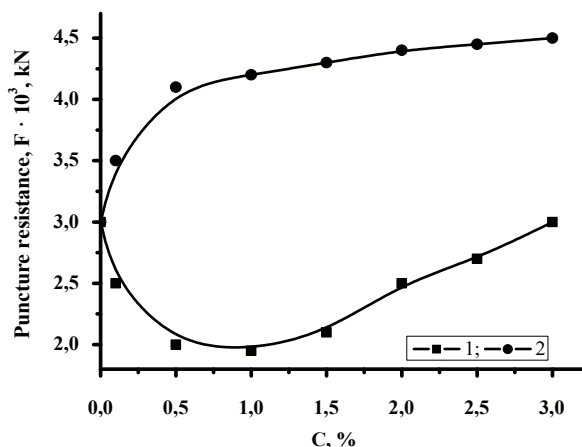Fig. 5. Effect of metal ions on the elasticity modulus of starch-agar biofilms at *m*=2.5: 1 – Ca^{2+}; 2 – Mg^{2+}

Fig. 6. Effect of metal ions on puncture resistance of starch-agar biofilms at m = 2.5: 1 – Ca^{2+}; 2 – Mg^{2+}

The curves of the dependence of the elastic modulus of films on the concentration of Ca^{2+} and Mg^{2+} ions pass through the maximum (Fig. 5), which is also most pronounced in the case of Mg^{2+} ions.

When measuring the puncture resistance of films (Fig. 6) obtained in the presence of different concentrations of Ca^{2+} and Mg^{2+} ions, it was found that even small amounts (0.1–1.0 %) of these metals have different effects on this characteristic. Ca^{2+} ions first reduce and then increase the amount of puncture resistance; in the presence of Mg^{2+} ions, the film puncture resistance first increases sharply, then becomes unchanged.

5. 4. IR spectroscopy of films

To obtain information about the biodegradation of films based on starch and agar, an IR spectroscopic study was performed. Fig. 7, 8 show the IR spectra of the films after they are stored in the air for 1 and 7 days.

On the IR spectrum of the starch-agar film after 1 day of storage, a wide absorption band is noticeable at the oscillation frequency of 3,400 cm^{-1}, due to OH groups of 2 polysaccharide molecules. Further, at values of ν 2,932 cm^{-1}, 1,671 cm^{-1}, peaks corresponding to the valence fluctuations of C – H groups were found; at 1,373 cm^{-1}, a peak due to asymmetric valence fluctuations of sulfo groups in the RO-SO2R' fragment of agar macromolecules appears. At a value of ν 1,412 cm^{-1}, a peak corresponding to the strain fluctuations of the C – H bond is shown [14].

The peaks detected at the oscillation frequencies of 1,187 cm^{-1} and 1,046 cm^{-1} belong to the C – OH, $CH_2O – CH_2$ bonds. In general, this region corresponds to the vibrations of the entire skeleton of the polysaccharide molecule. At values of ν 800–700 cm^{-1}, C – C and C – H bonds of hydrocarbons are detected.

After storing the films in the air for 7 days, the band expands noticeably at 3,400 cm^{-1} and the peak intensity decreases at 2,932 cm^{-1}. This may be evidence of the destruction of H-bonds as a result of evaporation of water molecules from the films. Instead of peaks at ν 1,412 cm^{-1}, 1,373 cm^{-1} and 1,187 cm^{-1}, a single wide peak of 1451 cm^{-1} appears. Such changes in the IR spectrum of films can be caused by changes in the number of C – H, C – OH, $CH_2O – CH_2$ bonds involved in the formation of the film. Also, after 7 days, the peak disappears at 1,373 cm^{-1}, corresponding to the agar sulfo groups. Peaks in the range of 1,000-500 cm^{-1}, corresponding to C – OH, C – C, and $CH_2O – CH_2$ bonds, undergo significant changes. This indicates that the skeletons of starch and agar polysaccharide molecules undergo changes during storage. In general, changes in the spectrum in the frequency range of 1,300 – 500 cm^{-1} indicate changes in the skeleton of carbohydrate molecules. Such changes may be the result of breaking the chain of C – C bonds in macromolecules of biopolymers with the formation of shorter-chain fragments.
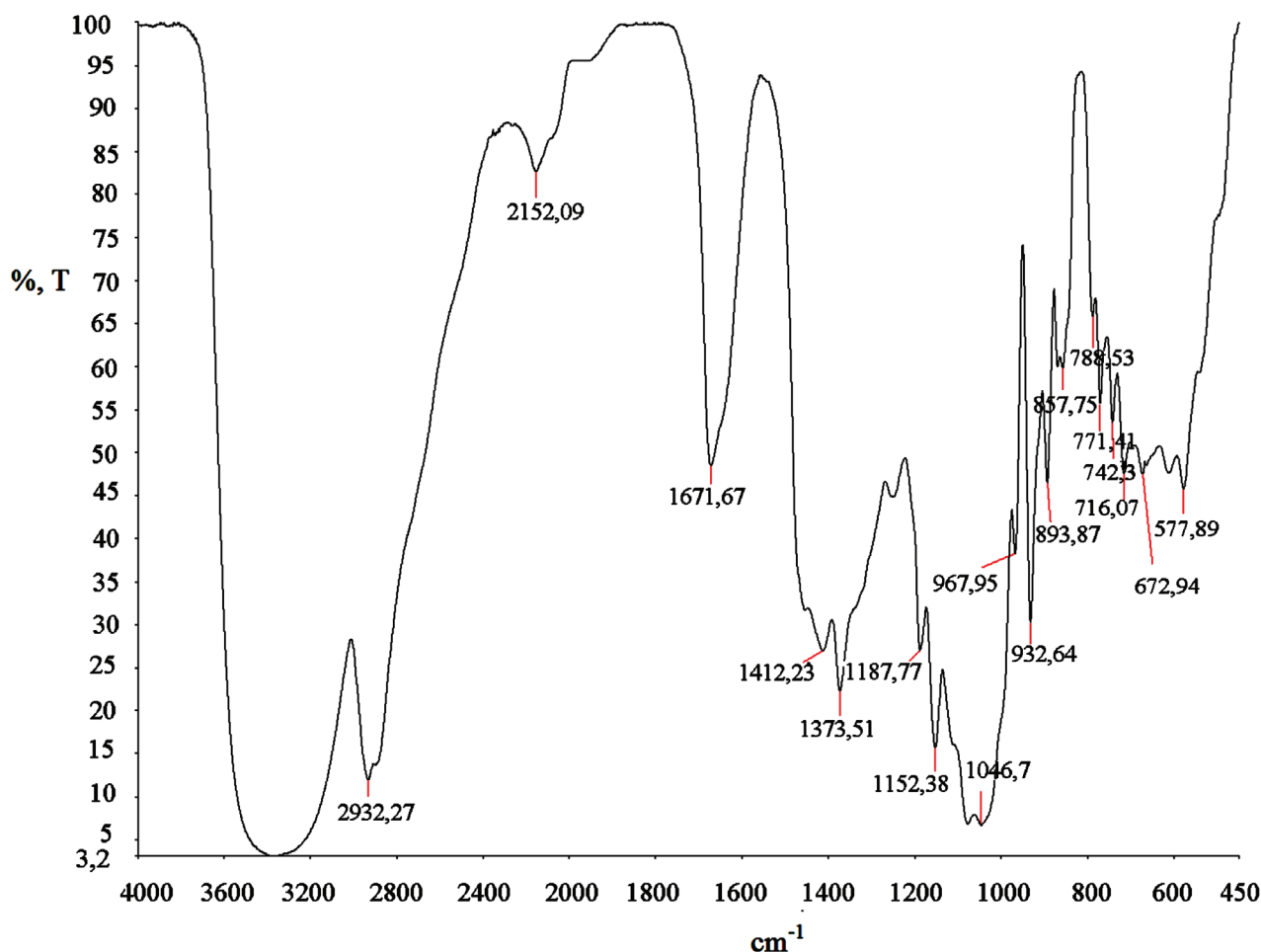

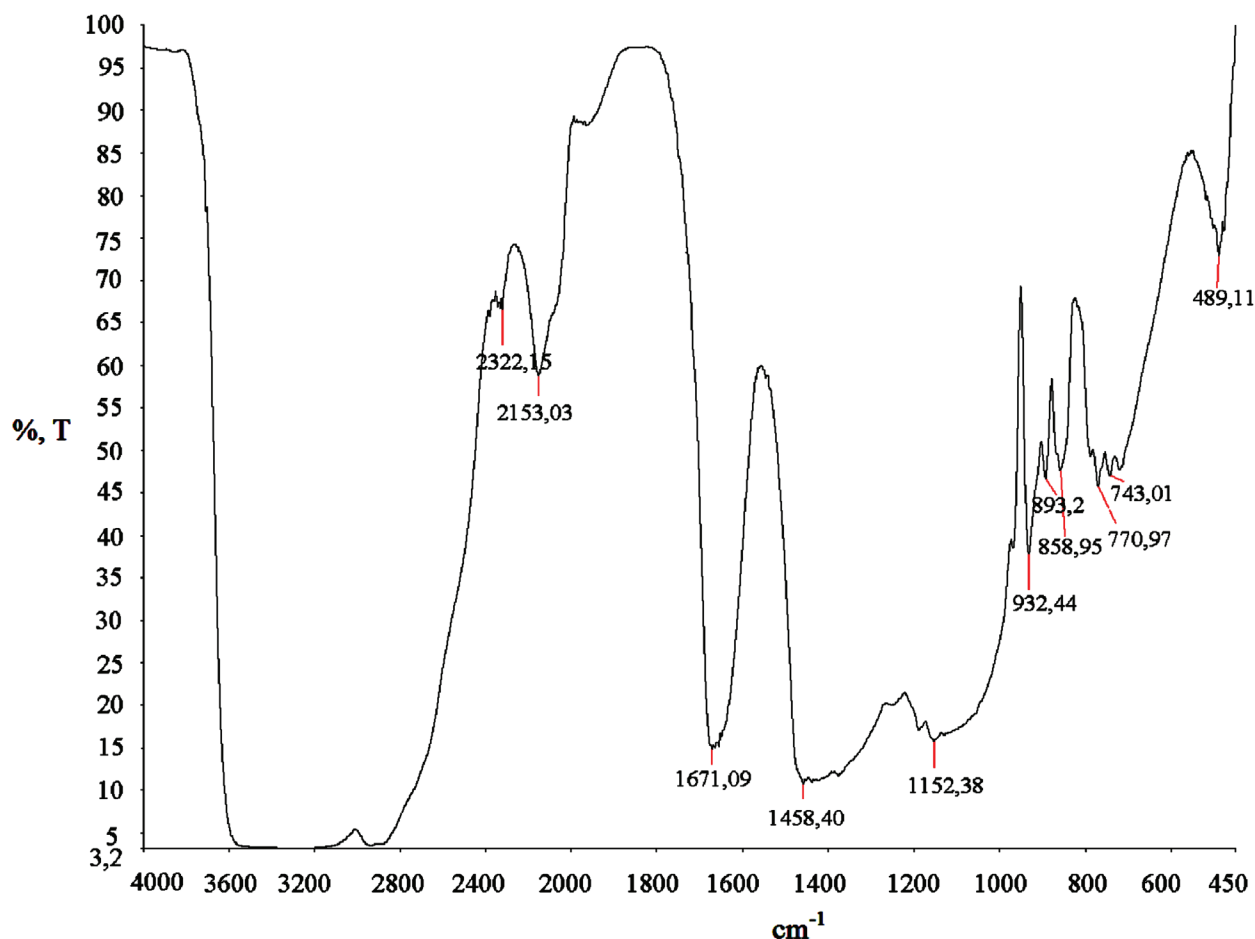Fig. 7. IR spectrum of the starch-agar film obtained at m=2.5

Fig. 8. IR spectrum of the starch-agar film at m = 2.5, after 7 days of storage

6. Discussion of results

6. 1. Obtaining of films based on starch and agar

Starch is a polysaccharide consisting of a linear polymer – amylase and a branched polymer – amylopectin. Its use in the food industry is based on its ability to structure formation, it is a good food thickener, stabilizer of emulsion food systems, designated E1401–E1405. In pharmaceuticals, starch is used as a filler, a molding component [15].

At the same time, it should be noted that starch in the absence of other ingredients does not give such strong gels as, for example, gelatin or casein. For comparison, it should be noted that the critical structuring concentration of starch is 4 %, gelatin – 1 %, and agar – 0.4 % [16, 17]. It follows that a relatively high concentration (at least 4 %) is required for structuring starch.

To obtain films, mixtures of starch and agar were used at different mass ratios, in which glycerin was introduced as a plasticizer. The resulting films are homogeneous, have no foreign inclusions and are easily separated from the glass surface. If we consider films obtained from individual polymers in the presence of a plasticizer, then starch films are very brittle, and agar solutions do not spread on a solid surface. Mixing solutions of 2 polymers in the presence of glycerol leads to the elimination of these disadvantages and the formation of more elastic films than in the case of starch and agar separately. However, it should be noted that exceeding the amount of added glycerol 2 %

of the mixture leads to an increase in the hygroscopicity of the films. This makes them difficult to dry and separate from the hard surface. Therefore, the glycerol content in all experiments was constant and equal to 2 %. Thus, the peculiarity of the method for producing films based on starch and agar consists in mixing their solutions at different ratios, adding glycerol, mixing, pouring on a glass surface and storing for 24 hours.

6. 2. Structural-mechanical properties of starch-agar films

Although both polymers used to produce films – agar and starch – are polysaccharides, their tendency to structuring is different. In both polymers, the main interactions underlying structuring can be hydrogen bonds between – CH_2OH and – OH groups of carbohydrate macromolecules, stabilized by hydrophobic interactions between their nonpolar parts. However, the higher structure-forming capacity of agar may also be due to the formation of a double helix by agarose macromolecules, which is prone to the formation of H-bonds [17]. In general, the formation of films can be explained by the participation of agar macromolecules, starch and glycerol molecules in the formation of a grid of hydrogen bonds between their polar groups and hydrophobic interactions between non-polar sections of their molecules. Moreover, these interactions can be either intermolecular or intramolecular.

Low values of the strength of the obtained films (Fig. 1) in comparison with the known ones [13, 18] may be due to

the fact that the total concentration of starch and agar in the mixture for producing films does not exceed 4 %. In addition, the structure formation in the studied system is caused by weak non-covalent interactions: H-bonds and hydrophobic interactions whose energy does not exceed 10 kJ/mol [19]. In the case of films obtained and described in [13], no solvents were used to dissolve the initial polymers. In this work, a mixture of 1 kg powdered cassava starch, 2 kg polyvinyl alcohol liquid, 100 g talc powder, 100 g urea and 400 ml of glycerol was stirred to yield a semi-dry powder. Thereafter, the mixture was extruded with a film extruder to produce a biodegradable film. The films are obtained not from polymer solutions, but from mixtures of a thicker consistency, which, accordingly, provide high strength of the films. However, it should be noted that although the strength of starch-agar films (2.3–2.8 kPa or 0.0023–0.0028 MPa) is significantly inferior to the films described in the literature [13], they are close to the confectionery masses for packaging which they can be used (0.0022–0.0045 MPa) [20].

The role of non-covalent interactions of 2 polysaccharides in the formation of films is evidenced by data on determining their roughness (Fig. 3). If the height of the peaks corresponding to the size of polymer clots in starch films is 200 nm, then after mixing with agar, it is reduced to 30 nm. This may be the result of the interaction of two polymers and solubilization of polymer clumps in their hydrophobic parts.

The difference and advantage of the method used to produce starch-agar films is the low concentration and, consequently, consumption of the initial polymers.

6. 3. Effect of Ca^{2+} and Mg^{2+} ions on structural-mechanical characteristics of starch-agar films

An effective way to regulate the structural and mechanical properties of biodegradable films is to introduce additives that affect the chemical and non-covalent interactions of the polymers that make up them. Such substances can be cross-linking agents, stabilizers, plasticizers, dyes, salts, etc. From this point of view, Ca and Mg compounds are of particular interest, which can have a cross-linking effect on agar and starch macromolecules. On the other hand, Ca and Mg are biogenic elements and can be incorporated into food in small amounts. Given that films are intended for food packaging, small amounts of Ca^{2+} and Mg^{2+} ions can be introduced into them. In this regard, the influence of Ca^{2+} and Mg^{2+} ions on the structural and mechanical properties of starch-agar films has been studied.

Fig. 4–6 show the curves of dependence of structural and mechanical characteristics of starch-agar films on the concentration of salts of Ca^{2+} and Mg^{2+} ions. Data from these figures show that the effect of Ca^{2+} and Mg^{2+} ions on the strength, elasticity and puncture resistance of films is very different. In the case of Mg^{2+} ions, there is an extreme dependence of the strength and deformation characteristics of the films on the concentration of the introduced salt. The introduction of Ca^{2+} ions into the system, as expected, leads to a monotonous growth of these characteristics.

The obtained results indicate a difference in the mechanism of action of Ca^{2+} and Mg^{2+} ions on structure formation in the starch-agar system. This difference is most clearly shown in the curves of changes in the film puncture resistance when the concentration of alkaline earth metal salts varies (Fig. 6). If in the presence of 0.1–1.0 % Ca^{2+} ions there is a sharp decrease in the value of puncture resistance, then Mg^{2+} ions cause a sharp increase in this characteristic.

To explain the observed phenomenon, consider the literature data. In living organisms, Mg^{2+} ions are antagonists of Ca^{2+} ions [21]. Mg^{2+} ions are intracellular ions, and Ca^{2+} ions are extracellular. Mg^{2+} ions, as ions with a high charge density, strengthen the structure of water, and Ca^{2+} ions, as ions with a low charge density, destroy the structure of water. In this case, Mg^{2+} ions should help strengthen the H-bond grid in the structured system and their costs to achieve high strength will be minimal, while Ca^{2+} ions destroy the hydrogen bond grid, which is the basis for structuring the system. From this, the advantage of using Mg^{2+} ions to strengthen the structure of starch-agar films is obvious. At the same time, it is likely that both Ca^{2+} and Mg^{2+} ions cross-link the macromolecules of two polysaccharides in the $– OH$ and $– OSO_2$ groups.

6. 4. Biodegradation of starch-agar films

One of the main characteristics of the resulting films is their biodegradability. Ideally, the final products of biodegradation should be carbon monoxide and water. A substance or product has good biodegradability if it is completely decomposed in 6 months. Intermediate products of biological decomposition will be short-chain hydrocarbons, the dynamics of changes in their concentration can be studied by methods of physical and chemical analysis. Various methods are used to test the biological decomposition of films. This is the action of microorganisms on the film material, burying films in the soil for some time and measuring the loss of film mass, etc. In this paper, the method of IR spectroscopic analysis is used to assess the biodegradability of films.

Analysis of the IR spectrum of the starch-agar film (Fig. 7), where the most pronounced peaks were found at the oscillation frequency of 3,400 cm^{-1}, due to the OH groups of 2 polysaccharide and glycerol molecules, suggests that the determining role in the structure formation in the starch-agar system is played by H-bonds. In the range of values of ν 2,932 cm^{-1} – 1,412 cm^{-1}, peaks corresponding to valence and strain fluctuations of the C – H bond are detected, and in the region of ν 800 – 700 cm^{-1}, C – C and C – H bonds of hydrocarbons are detected, which can provide hydrophobic interactions between non-polar sections of macromolecules of two polysaccharides. It should be noted that it is the participation in the structure formation of weak non-covalent interactions: hydrogen bonds and hydrophobic interactions that can cause the biodegradability of films.

Storage and study of starch-agar films for 7 days showed significant changes in the intensity and localization of peaks corresponding to O – H, C – H and C – C bonds (Fig. 8).

The most noticeable changes were found in the left part of the spectrum at the oscillation frequency of 3,400 cm^{-1}, which may be due to the destruction of H-bonds between macromolecules of 2 polysaccharides. Changes associated with the destruction of the hydrocarbon chain include changes in the intensity and position of peaks at ν 2,932 cm^{-1}, 1,671 cm^{-1}, 1,412 cm^{-1} and 1,187 cm^{-1}, corresponding to the valence and deformation vibrations of C – H and C – OH bonds; also, after 7 days of film storage, the peak at 1,373 cm^{-1} corresponding to the agar sulfo groups disappears.

In addition, significant changes in the IR spectrum of starch-agar films occur in the range of oscillation frequencies of 1,000 – 500 cm^{-1}, corresponding to C – OH, C – C and $CH_2O – CH_2$ bonds. This indicates that the skeletons of macromolecules of starch and agar polysaccharides undergo

changes during storage. Such changes may be the result of breaking the chain of C – C bonds in macromolecules of biopolymers with the formation of shorter-chain fragments.

In general, the observed changes in the IR spectrum of starch-agar films after storage may be evidence of their biological degradation due to the destruction of the grid of hydrogen bonds and hydrophobic interactions, as well as the break of hydrocarbon chains and the destruction of the skeleton of carbohydrate molecules.

Thus, at different mass ratios of the initial reagents, biodegradable films based on starch and agar were obtained. They can be used for packaging food products, in particular, confectionery. The advantages of the developed method for producing films include simplicity of execution and low consumption of initial reagents. The method does not involve the use of expensive equipment, compliance with special conditions, such as maintaining a constant temperature, pressure, pH, etc. In addition, the use of cheap raw materials – starch and agar – causes a low cost of the final product.

The disadvantages of the study include the lack of information about the effect of glycerol used as a plasticizer on the structural-mechanical properties of films. In addition, a wider time interval could be used to control biodegradation.

The limitations of the study are that more diverse source polymers and food additives could be used to give the films the desired properties. Special attention should be paid to microbial polysaccharides [22]. Due to the growing interest in obtaining edible food packaging, research should be conducted to regulate the taste of films. It is also necessary to test the films as packaging of real food products.

The prospect of developing research in this direction may be related to the expansion of methods for studying the properties and justification of the biodegradability of films. In addition, to regulate the strength and elasticity of the films, cross-linking agents, surface-active substances used in the food industry, etc. can be used. Such a detailed study of the possibility of regulating the structural and mechanical properties of films can expand the scope of their application (pharmaceuticals, cosmetics, etc.). However, this may lead to difficulties in selecting the starting reagents for producing edible films, as some dyes and flavorings may not be allowed to be included in food packaging.

7. Conclusions

1. By mixing solutions of starch and agar at different mass ratios of polymers, biodegradable films are obtained. Their structural and mechanical characteristics are determined. It is shown that the values of the strength, modulus of elasticity and puncture resistance of films are maximal at the mass ratio of agar/starch m, equal to 7–9.

2. Effect of Ca^{2+} and Mg^{2+} ions on the strength and deformation characteristics of biofilms was studied. It is shown that Ca^{2+} ions monotonically increase the strength characteristics of starch-agar films, while the curves of changes in these parameters in the presence of Mg^{2+} ions have maxima at a concentration of 0.5 %. The difference in the effect of Ca^{2+} and Mg^{2+} ions on the strength and deformation characteristics of films is justified by the different hydration of these ions. Mg^{2+} ions contribute to the structuring of the system by strengthening the H–bond system, and Ca^{2+} ions destroy H–bonds, although they cross-link carbohydrate macromolecules via – COOH and – OH groups.

3. Biodegradability of starch-agar films was monitored by the change in their IR spectra. It is shown that the most significant changes are observed in the intensity and localization of peaks corresponding to O – H, C – H and C – C bonds, which can be evidence of changes in the structure of films caused by the destruction of the grid of hydrogen bonds and hydrophobic interactions, as well as the break of hydrocarbon chains and the destruction of the skeleton of carbohydrate molecules.

Acknowledgments

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