

Представлено результати дослідження впливу термотропних полісахаридів та гліцерину на структурно-механічні властивості альгінат-кальцієвих оболонок продукції капсульованої з внутрішнім жировим умістом. Установлено, що введення пектину низькоетерифікованого, агару та гліцерину призводить до зниження модуля пружності та збільшення модуля еластичності гелевих систем на основі альгіната кальцію. Результатом цього є збільшення коефіцієнту проникності оболонок капсул, що дозволяє контролювати вологоутримуючу та вологовиділяючу здатність оболонок капсул для забезпечення заданих органолептичних показників інноваційної продукції

Ключові слова: альгінат-кальцієва оболонка, напівфабрикат харчовий жировий капсульований, іотропне-термотропне гелеутворення

Представлены результаты исследований влияния термотропных полисахаридов и глицерина на структурно-механические свойства альгинат-кальциевых оболочек продукции капсулированной с внутренним жировым содержанием. Установлено, что введение пектина низкоэтерифицированного, агара и глицерина приводит к снижению модуля упругости и повышению модуля эластичности гелевых систем на основе альгината кальция. Результатом этого является увеличение коэффициента проникновения оболочек капсул, что позволяет контролировать процессы гомеостаза. Полученные данные дают возможность корректировать влагоудерживающую и влаговыводящую способность оболочек капсул для обеспечения заданных органолептических показателей инновационной продукции

Ключевые слова: альгинат-кальциевая оболочка, полуфабрикат пищевой жировой капсулированный, иотропно-термотропное гелеобразование

A STUDY OF THE EFFECT OF THERMOTROPIC POLYSACCHARIDES ON THE PROPERTIES OF THE ALGINATE-CALCIUM SHELL OF AN ENCAPSULATED FATTY SEMIFINISHED FOOD PRODUCT

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1. Introduction

An analysis of recent trends in food science shows the widespread use of macromolecular compounds (MMCs), including polysaccharides [1, 2], in food technology. From the point of view of constructing the primary technology and the requirements for the quality of the final product, they must be characterized by technological stability and harmlessness. At the stages of consumption and digestion, they must not spontaneously form new compounds both in the technological flow and at the stage of creating the formulation, during the high-temperature treatment, etc. Such predictions can be explained by the fact that polysaccharides are characterized by the presence of active groups capable of

intermolecular association in the molecules, changes in the spatial structure, a hydrophilic-lipophilic balance, and salivation. The main types of communication, which occur and simultaneously provoke changes in the technological flow, are ionic, ion-dipole, hydrogen, hydrophobic, etc. [1]. The structure of MMCs has crystalline zones that determine the strength of their films (coatings) and the amorphous zones in which the macromolecule exhibits high mobility during swelling. In swollen hydrogel polysaccharide systems, low molecular weight nutrients are released, accompanied by the effect of a varied, uncontrolled dosage. The use of MMCs that are capable of controlled swelling under different conditions can purposefully change the technological and texture characteristics of the product and the kinetics of nutrients

penetration through polysaccharide shells of structured products. Low diffusion rates through the hydrogel provide the effect of prolonged assimilation, whereas high rates make it more intense. Therefore, the selection of compositions (participants) of the hydrogel capsule shell formation, in addition to the organoleptic properties of the final product, also has a physiological significance.

The use of natural polysaccharides in the technology of encapsulated fatty semifinished food products (EFSFFPs) can help produce effective systemic benefits of fat encapsulation. This is achieved as a result of implementing the technological principles of the emergence of a fundamentally new form – factually, in the state of a controlled dose by the mass. Due to this, the volume of consumption is easily and effectively controlled, and the presence of biologically active groups of polysaccharides promotes the assimilation of the product as a whole. In the framework of scientific research, the key component of the technological process of making encapsulated products with an internal fat content is alginic acid in the form of a soluble salt of sodium alginate (AlgNa). Alginic acid consists of the residues of β -D-mannuronic and α -L-guluronic acids, which are linked by 1-4-glycoside bonds [2]. From a chemical point of view, AlgNa is capable of forming thermostable gels, including film-like edible shells, in the presence of divalent cations, in particular calcium [3]. The use of EFSFFPs in the food industry is primarily related to their commodity-technological characteristics. This, in turn, is affected by the properties of the alginate-calcium shell and the fat content. The shell properties should be understood as a complex of structural, mechanical and texture characteristics with the ability to react to or restrain external technological or controlled impacts.

These predictions suggest the need for a scientific substantiation of a set of technological measures to provide a controlled modification of the properties of EFSFFP shells.

2. Literature review and problem statement

The structure-forming properties of alginates during the addition of crosslinking salts can be adjusted in the direction of enhancing or weakening the elastic properties of the gel, which is very important from the organoleptic and texture points of view. This is due to adding substances that are capable of creating a spatial mesh in a solvent under certain conditions or of forming complexes with Alg_2Ca [2, 4]. However, at the same time, it is important to take into account the physical and chemical behaviour of multicomponent technological systems. That is, it is necessary to create a soluble system in advance for it to contain at least two polymers in a common solvent.

By colloidal properties, the requirements for the developed solutions in the general formula are formed by the possible phase behaviour of a mixture of polymers in the solution. The result may be a phase bundle of the system or a thermodynamic compatibility of polysaccharides in a solution with colloidal signs of homogeneity. According to the Flory-Huggins theory of mixtures of polymers for the three-component systems “polymer–polymer–solvent”, which are created in a technological flow, there can be two types of phase separation – segregative and associative [5].

With the segregation type of the system, there are solutions that are characterized by the presence of at least two polymers, usually neutralized. Due to the presence of repul-

sive forces or different ratios of the polymer to the solvent, solutions may be incompatible. Essentially, in the presence of one solvent in the system, there are two solutions, each of which is enriched with one of the food polymers. At the same time, there is a certain amount of a homogeneous solution that dissolves both polymers, but one of them is in surplus in relation to the other. In fact, two non-mixing solutions are formed in such a composition. This type arises as a result of the colloidal behaviour of the dissolved substances in the implementation of control or perturbing factors. Accordingly, during the provision of the “sol-gel” phase transition, the gel-like system will be represented by two independent meshes whose interaction with and influence on the properties of the gel can only be determined experimentally [3, 5].

In the presence of two ionotropic polysaccharides in the solvent, but having opposite charges, the mutual gravity of the polymer with the bundle of the associative type system may arise. Moreover, there may occur insoluble complexes and, during gelation, mixed gels with a “chemical” structure of the meshes.

There are four types of systems that can be used to modify the shells of capsules, which include a common solvent and two food polymers:

a) A solution of uncharged (neutral) polymers. It cannot be used in the EFSFFP technology, since the gel initiator sodium alginate (AlgNa) refers to ionotropic polysaccharides. However, in its structure, there are polymeric areas that do not carry the charge. The solution of a neutral polymer and an electrolyte is thermodynamically compatible with mixing without phase separation and deposition. The solution is able to increase viscosity compared to monocomposition systems due to the association of polymers as the result of forming hydrogen bonds. The stability of the binary solution is ensured by the polyelectrolyte expansion in the solvent, which provides the formation of a homogeneous mixture of the solution with a neutral polysaccharide. In the case of gelation due to the neutralization of the electrolyte (in our case, the formation of the Alg_2Ca gel), the process system can be split into two non-mixing phases. That is why gelling must occur simultaneously with the formation of the final product (in our case, the formation of a spherical form of the capsule) [6]. Polyelectrolytes are polymers containing ionogenic groups that acquire a charged form in aqueous solutions due to the dissociation of functional groups. Then the macromolecule is in the state of a polyanion around which there is an equivalent number of counterions. Polyacids are transferred to this state, and the elements formed are polyanions and polyulages – polycathions, polyampholytes, polycyclic acids, etc. [1, 3, 6]. By the degree of dissociation, such solutions are distinguished as strong (ionization does not depend on the pH of the medium) and weak (which are capable of partial ionization). Alginates belong to weak polyacids [5].

b) Technological systems that contain the same charged polyelectrolytes and are characterized by thermodynamic incompatibility. The segregation type of such systems leads to phase separation. The use of such hydrocolloids dissolved in a common solvent in a process flow is complicated. However, in the presence of a blocking charge of inorganic salt or a polyelectrolyte in the gel formation system, gel formation may occur with the emergence of a complex gel mesh.

c) Systems with oppositely charged electrolytes through a common solvent. Such systems are problematic for modifying the shells of capsules, since electrostatic attraction through the medium of a common solvent will lead to

the formation of associative complexes with strong bonds. They are formed as a result of cooperative reactions. These complexes in scientific sources are called polyelectrolytic complexes, PECs [7]. The emergence of an interchain saline connection facilitates the formation of bonds between PEC cells, which can arise due to the addition of a third substance – a blocking polyelectrolyte. Such a combination of electrolytes in a common solvent provides these complexes with high stability in the process flow and during storage of structured products.

d) A solution of unmixed polymers. In this case, however, the formation of such a solution is impossible, since AlgNa ionotropic solutions are the key and compulsory gelling agent.

In previous studies [8, 9], the ionotropic gelation was used in the EFSFFP technology to form the capsule shell. Under these conditions, the process of forming the structure of the EFSFFP is implemented on the principle of compensation of the chemical potentials of the recipe components of the technological system, that is, AlgNa and Ca^{2+} . However, this may result in a serious shortage of new products, for example, during the introduction of capsules into the technological medium, which has an obvious impact on the stability of the cooperative ties of the alginate-calcium coagulant. Such properties exist in saline, aqueous solutions, technological systems with extreme pH values or technological combinations. The expressed disadvantage of the compounds is their “rigid” design, which in technological terms is identified by the low plasticity of the system. In the state of films, which is typical for shells of capsular products, the external deformations applied to them lead to the destruction of the capsule. Such cases can occur, for example, during mixing viscous media such as meat, fish stuffing, certain types of dough, during mixing with crushed texture, puree ingredients, etc. The result of the low elasticity of the alginate-calcium shell is the inability to react to the external load by the internal high-elastic deformation or the limited flow within the limits of Hooke's loads [10]. From the commodity-technological point of view, such shortcomings of the capsule should be evaluated as a decrease in the qualitative characteristics of the finished product. On the other hand, the high thermal stability of EFSFFPs, as an obvious technological advantage over capsules with thermotropic membranes, requires some controlled adjustment at some technological and physiological points – for example, during the penetration into the middle of the capsule of digestive ferments, or during the provision of diffusion flows in or from intact technological environments.

With neutral polysaccharides (for example, agar) the AlgNa solution is mixed in unlimited quantities, and the presence of a significant amount of counterions (Na^+) leads to an increase in the entropy of the dissolution. Mutual repulsion of anions in the solution promotes the formation of a homogeneous system of two polysaccharides in the solvent. Such systems, depending on the degree of neutralization, can be split into a segregational or associative type. It is obvious that the regulation of the characteristics of the capsule shells of EFSFFPs is possible through the use of different properties of modifiers-polysaccharides and the regulation of the properties of the solvent.

3. The aim and objectives of the study

The aim of this study was to research the effect of agar, low-esterified pectin and glycerol on the structural and

mechanical properties of formulations based on AlgNa and alginate-calcium capsule shells in the EFSFFP technology.

To achieve this aim, the following tasks were solved:

- to investigate the influence of model AlgNa-based systems on the structural and mechanical parameters, taking into account the peculiarities of the structure, physicochemical parameters and heat-resistant features of polysaccharides and glycerol;

- to study textural properties of the alginate-calcium shell of a capsule under the conditions of mixed ionotropic and thermotropic gel formation.

4. Materials, objects and methods of the study

4. 1. Materials and objects of research

The objects of the study were model systems based on AlgNa; formulations based on AlgNa and low-esterified pectin or agar or glycerol; Alg₂Ca gels; mixed gels based on Alg₂Ca and low-esterified pectin or agar or glycerol.

The recipe mixture during the production of capsule shells was made as follows: after swelling in water, the prepared “low-esterified pectin and water” or “agar and water” mixture was heated to a temperature of $t=92...95\text{ }^\circ\text{C}$ and held so until the polysaccharide was completely dissolved. Afterwards, the hot solution of the polysaccharide was combined with a solution of AlgNa in the calculated proportions to obtain a recipe mixture at a temperature of $t=(62...65)\pm 5\text{ }^\circ\text{C}$. The solution in the process flow was tempered to prevent phase banding and polysaccharide hydrolysis. To prepare the model systems with glycerol, the AlgNa solution was combined with glycerol and stirred until a homogeneous system was obtained. Table 1 shows the initial concentrations studied.

Table 1

Initial concentrations of thermoionotropic polysaccharides and glycerol in a recipe mixture based on AlgNa ($C_{\text{AlgNa}}=1.0\text{ }%$)

No.	Name of substance	Concentration of matter, %
1	Agar	0.4; 0.5; 0.6; 0.7; 0.8
2	Low-esterified pectin	2.0; 3.0; 4.0; 5.0; 6.0
3	Glycerol	0.5; 0.75; 1.0

To obtain encapsulated systems with internal fat content, the recipe components were subjected to drip extrusion through a vertical two-pipe head of the extruder of the device UZhK-20 (Ukraine) [11, 12] in the medium of an aqueous solution of CaCl_2 .

4. 2. Methods of researching structural and mechanical properties of model systems based on AlgNa

The viscosity of the solutions of AlgNa and of the mixed model systems subject to encapsulation were studied on the viscometer VPN-0.2M at a constant shear stress [13].

The structural and mechanical properties of Alg₂Ca gels and mixed gels were determined with the help of modified Kargin-Sogolova scales by studying the deformation (pliability) during compression of the model systems by the action of a punch under constant stress [13]. Sufficiency refers to the ratio of deformation to the continuous stress. In this approach, under conditions of linear behaviour, sufficiency is the constant of the investigated material and it does not

depend on the applied stress. The rheological values of the model systems were calculated by analysing the yield curve.

5. Studying the influence of thermoionotropic polysaccharides and glycerol on the textural indicators of model systems based on AlgNa

5. 1. Studying the influence of polysaccharides and glycerol on the structural and mechanical parameters of aqueous solutions of AlgNa

It is predicted that the joint use of ionotropic and thermotropic gelation with given functional properties can substantially modify the properties of the EFSFFP shell. The conditions of providing the substantiated principles of the technological process of capsule formation help expand the technological capabilities of the new product in the technology of food and culinary products. Agar and low-esterified pectin as the formulation components that are thermodynamically compatible with an aqueous AlgNa solution [14] are used as capsule shell modifiers. Also, the effect of glycerol is studied in highly soluble alcohol, which does not salt out soluble polysaccharides at concentrations up to 5.0 % [5, 8].

This approach is based on the prediction that controlled gelation will result in the formation of a mixed gel the common properties of which will be proportional to the contribution of the partial properties of the formulation components. At the same time, the technological properties of the gel-like ionotropic and thermotropic system will be determined by an additional mesh of hydrogen bonds and electrostatic interactions. Moreover, they will be characterized at the molecular level by the presence of values of the size of hydrophobic parts that are formed by salt bridges and coordination bonds.

It is evident that the microstructure of the mesh of a gel in the conditions of ionotropic and thermotropic gelation will depend on the temperature of the process of capsule formation. When the conditions of thermotropic gel formation and ionotropic gelling are met, the gel framework will have the structure of a thermotropic gel. Conversely, ionotropic gel meshing will occur in the first stage during the capsulation at higher temperatures of thermotropic gel formation. Then, during cooling, it will be “flashed” with an additional mesh of thermotropic gel.

The effect of modifying the properties of the capsule shell is derived from the phase behaviour of a mixture of polymers, and it is described by a phase diagram that characterizes the conditions of occurrence and composition of phases as described above.

Under conditions of thermodynamic combination of agar or low-esterified pectin according to the Flory-Huggins theory of mixtures of polymers [5] in the three-component system “polymer A (AlgNa) – polymer B (polysaccharide) – solvent (water)”, it is possible to obtain a segregation type gel with a mutually permeable gel mesh. It is probable that in the conditions of thermodynamic compatibility there will comprise two independent gel meshes with the formation of zones with nonspecific interaction.

Under conditions of using a shell of triatomic alcohol as a modifier, it is envisaged to obtain one of the types of gel but with increased plastic properties due to the chemical and colloidal inertness of alcohol. In this case, the alcohol should not have dehydrating properties and, at the same time, it should not be solvent of salts. In addition, it should be taken

into account that the use of alcohols in the technology of EFSFFPs as a diluent of the solvent leads to significant changes in the rate and physical mass of the capsule shell growth.

The need to modify EFSFFP shells is based on several prerequisites that are formulated from two features. The first feature is formulated from the prediction of the use of EFSFFPs in food and cooking products, which is subjected to various technological influences, namely:

- temperature at intervals that are typical of the traditional technological flow (about 100 °C) in various aqueous media or in a steam-water mixture. It is necessary to take into account the possibility of using EFSFFP in the media of recipe mixtures and semifinished food products – ground meat, sauces, garnish and various types of dough, which are subjected to heat treatment for a given time, that is, with the simultaneous influence of the binomial product $\tau \times t$;
- temperature influence in hydrophobic environments, when EFSFFPs are in a medium of oils and fats, which are the storage medium as well as the recipe components, for example, in the composition of dressings;
- technological influence of media with the expressed influence of chemical potentials in the form of ionic strength, pH of the environment, which is typical for sauces;
- mechanical, technological influence of different properties of technological systems.

The use of the low-esterified pectin membrane structure modification is based on many prerequisites. It is a necessity to modify the mechanical, structural and physicochemical properties, including thermal resistance as well as resistance to acidic pH values of the environment and the properties of the polysaccharide matrix of Alg_2Ca [10]. This, in turn, affects the loss of moisture by the gel system and the possibility to use a new product in various technological environments.

When using pectin in the study, its inbound functional properties were taken into account. The solubility was 119, the gelling ability was 119–122, the surface activities were 123 and 124, and the thermodynamic flexibility, which, depending on the esterification degree (ED), reached a maximum in the range of $43.0 < \text{CE} < 58.0 \%$ (119–125–127). As the ED value grew, its solubility increased simultaneously. In addition, account was taken of the fact that high-grade esterification pectins are capable of gelling in acidic media in the presence of sugar (the technology of dressings, sauces, and refills). Pectins of low esterification levels in the presence of polyvalent metal salts are capable of chemical interaction, which corresponds to the concentration of Ca^{2+} in the system [8, 10].

Agar, as a sulfated polysaccharide, is one of the phyto-cololides in gel-like food products. Agar has agarose and agarpectin in its composition. However, gelling of agar happens only at the expense of agarose by the formation of a “physical” gel – the structure of molecules due to hydrogen bonds. Each agar molecule in the gel structure is actually independent, so the formation of the gel structure is not a polymerization process. This means that hydrogen bonds essentially occur due to electrostatic interaction. In this case, the water (solvent) contained in the gel mesh is capable of relatively free movement in the middle of the gel macro-section [8, 10].

Glycerol does not typically dissolve different mineral salts, which means that pure glycerol in the system can affect only the solvent. Glycerol may remain liquid, and at temperatures below 0 °C its aqueous solutions behave in a

similar way. For example, a solution in which two parts by weight of glycerol correspond to one part of water freezes at a temperature of $t = -46.5\text{ }^{\circ}\text{C}$. Glycerol slows the formation of crystals of ice [8].

Since the technological mixtures for encapsulation in the EFSFFP technology should provide droplet capsule formation, viscosity and cogenesis were the key characteristics of the experimental solutions.

Fig. 1 shows the dependence of the concentration zones of aqueous solutions AlgNa on temperature. The temperature value is chosen taking into account the required flow of thermotropic polysaccharides through the capillaries of the forming heads of the extruder.

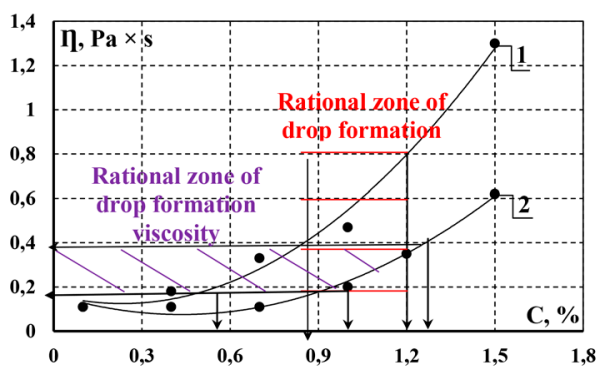


Fig. 1. The influence of temperature on the concentration zones of capsule formation in aqueous solutions of AlgNa of different concentrations: 1 – at a temperature of $t = 20 \pm 2\text{ }^{\circ}\text{C}$; 2 – at a temperature of $60 \pm 4\text{ }^{\circ}\text{C}$, respectively

In previous studies [2, 8, 9, 12], it was established that the viscosity of the input formulary mixture $\eta = 0.17 \dots 0.32\text{ Pa}\cdot\text{s}$ at a temperature of $t = 20 \pm 2\text{ }^{\circ}\text{C}$ is rational for the extrusion process. This helps obtain ready-made capsulated products with fatty contents with a diameter of capsules being $d = (5 \dots 8) \times 10^{-3}\text{ m}$ with high organoleptic characteristics.

The results of studying the viscosity dependence at different temperatures on the concentration of AlgNa indicate that in the range of rational concentrations of AlgNa, viscosity decreases 1.63 times. Such a dynamics occurs when the concentration ensures the process of drop formation ($C = 0.8 \dots 1.2\%$), given that the separation of a drop from the nozzle depends only on the viscosity of the solution. Such a significant reduction in the viscosity during heating allows for a significant concentration of pectin or agar. By maintaining the rational viscosity in the range of rational viscous mode ($0.17 < \eta < 0.32 \times 10\text{ Pa}\cdot\text{s}$), it is possible to produce a controlled effect on the properties of the shell for capsule formation.

When using a modifier additive in the form of agar, the working temperature of the extrusion must be higher than $t = 50\text{ }^{\circ}\text{C}$ [10, 14].

Fig. 2 shows the temperature-concentration dependence of the viscosity of agar solutions in the range of 1.0...4.0 %.

It was determined that at a temperature of $t = 60 \pm 2\text{ }^{\circ}\text{C}$ and the concentrations of the aqueous solution of AlgNa 1.0 % and agar $\leq 1.0\%$, the viscosity at different ratios is the same. The same pattern is observed during the receipt of algin-agar shells as well as agar-alginate membranes. However, the latter interpretation has significant factual constraints, since in the actual technological process there is a minimal critical concentration of AlgNa. The minimum concentra-

tion of AlgNa is responsible for the transformation of the colloidal unconnected formulation solution and the receiving medium of the Ca^{2+} solution, thereby providing capsule formation. During the experimental tests it was established that a decrease in the concentration of AlgNa in the system below the critical does not result in capsule formation, but a steady controlled mode arises already at AlgNa concentrations of $C \geq 0.8\%$.

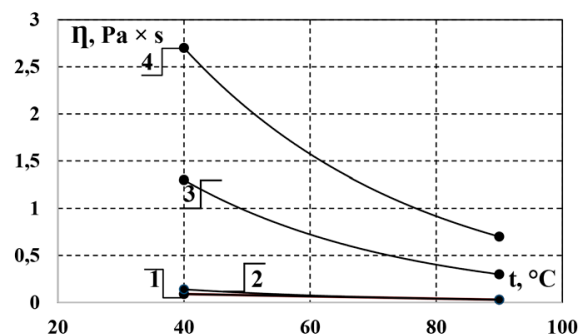


Fig. 2. Dependence of viscosity of the alginic-agar solutions on temperature at the concentrations of AlgNa $C = 1.0\%$ and agar, %: 1 – 1.0; 2 – 2.0; 3 – 3.0; 4 – 4.0, respectively

Since the initial condition is a temperature of $t \geq 60\text{ }^{\circ}\text{C}$, and the performance of the device for encapsulation does not allow rapid processing of recipe solutions, then the temperature colloidal stability of the recipe mixture is very important. As a rule, the result of thermal hydrolysis is a reduction in the viscosity of the mixture, which (indirectly) indicates the hydrolysis of polysaccharides and, as a result, the deterioration of the gel forming capacity and organoleptic characteristics of the EFSFFP. The study of the model systems of aqueous solutions of AlgNa subjected to thermocyclic degradation has established that due to the deterioration of the forming capacity of the polysaccharide, the technological costs in the production increase by 7.0...11.0 % for every 10.0 % decrease in the viscosity of the AlgNa solution when the relative viscosity ranges are 100.0–78.0 %, 18.0–26.0 %, and 78.0–55.0 %. Solutions in which the viscosity has decreased twice entail no formation. The tests have determined the regularities of the change in the viscosity of the technological algin-agar mixture (AlgNa – 1.0 %; agar – 0.4 %) during the thermostatic setting at temperatures of 70 °C, 80 °C and 90 °C (Fig. 3).

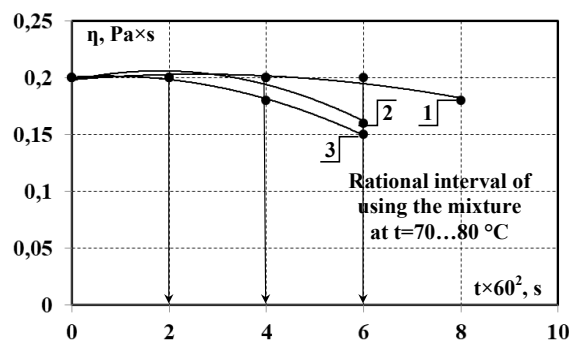


Fig. 3. The dynamics of viscosity of the alginovogo-agar mixture depending on temperature, C, at the concentrations of AlgNa 1.0 % and agar 0.4 %: 1 – 70 ± 2 ; 2 – 80 ± 2 ; 3 – 90 ± 2 , respectively

The research interval in the range of $\tau = (4 \dots 6) \times 60^2\text{ s}$ is selected taking into account the performance duration of

the device for encapsulation in real production conditions [11]. It has been confirmed that the technological stability of the work is about $\tau=6 \times 60^2$ s if the temperature is up to $t=70 \pm 2$ °C. However, it is reduced to $\tau=2 \times 60^2$ s for the thermostatic of the tested samples at a temperature of $t=90$ °C.

5. 2. Investigation of the influence of agar, low-esterified pectin and glycerol on the structural and mechanical parameters of Alg₂Ca gels

The dynamics of hydratibility of Alg₂Ca gels and mixed agar gels with AlgNa $C_{AlgNa}=2.0$ % concentration and agar in the range of $C=0.2...0.8$ % in the presence of Ca²⁺ (0.4 %) (Fig. 4) were studied.

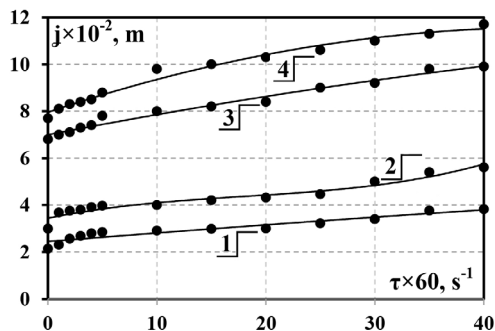


Fig. 4. Alg₂Ca gel creep curves at a temperature of $t=18 \pm 2$ °C, the concentration of AlgNa 2.0 %, the concentration of Ca²⁺ 0.4 %, and the concentration of agar, %: 1 – 0.8; 2 – 0.4; 3 – 0.2; 4 – 0, respectively

It has been determined that with increasing the content of agar in the system with a constant concentration of AlgNa there is a gradual decrease in the relative deformation of the mixed gels. The reason for this may be an increase in the particle size of the dry matter of the gelators and the corresponding appearance of the gel mesh. Fig. 5 shows the dependence of the highly elastic modulus of elasticity (E_{el}) and the degree of penetration of Alg₂Ca gels on the concentration of agar at a constant concentration of Alg₂Ca.

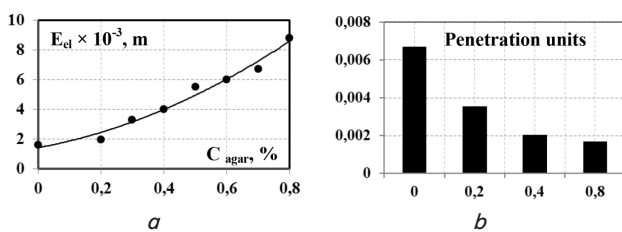


Fig. 5. Dependence of elastic properties of Alg₂Ca gels on agar concentration: *a* – modulus of elasticity ($E_{el} \times 10^{-3}$ m); *b* – degree of penetration (penetration units)

Analysis of Fig. 5 shows that the growth of the elastic modulus is practically linear. This is confirmed by the fact that there is no concentration interaction between the Alg₂Ca gel and agar gel. That is, in this case, in a mesh of one gel, a mesh of the other gel appears due to various mechanisms depending on the nature of the gelators. It can be stated that Alg₂Ca gels containing agar in the experimental concentration are characterized by greater elasticity than Alg₂Ca gels. This is due only to the concentration effect and the ability of agar to form a thermotropic gel mesh with its own structural and mechanical characteristics that influence the properties of the gel as a whole. The analysis of the main rheological characteristics of mixed gels based on Alg₂Ca and agar is given in Table 2.

Table 2 shows that the plasticity of the system increases more intensively, since the proportion of reverse deformation in the system is reduced from 82.5 to 68.0 % under conditions of growth of the concentration of agar up to 0.8 %. This confirms that the density of the mesh of the “chemical” Alg₂Ca gel is higher than the density of the “physical” mesh of agar gel. However, synergic interaction of the experimental structure formers has not been proved.

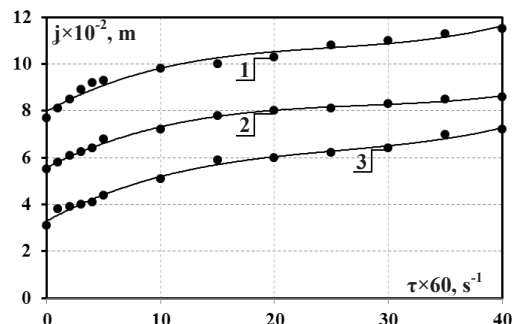


Fig. 6. Alg₂Ca gel creep curves at a temperature of $t=18 \pm 2$ °C, the concentration of AlgNa 2.0 %, the concentration of Ca²⁺ 0.4 %, and the concentration of pectin, %: 1 – 2.0; 2 – 1.0; 3 – 0, respectively

Table 3 shows the mutual influence of Alg₂Ca and low-esterified pectin as gelators on the properties of the resulting gel. The dynamics of a relative deformation of Alg₂Ca gels and mixed gels with pectin under conditions of the concentration of AlgNa $C_{AlgNa}=2.0$ % and pectin in the range of $C=1.0...2.0$ % in the presence of Ca²⁺ (0.4 %) (Fig. 6) were studied. It has been established that in the conditions of increasing the content of low-etherified pectin in the constant concentration of Alg₂Ca in the system, there is a gradual decrease in the patency of the model Alg₂Ca gels. The analysis of the main rheological characteristics of the gels (Table 3) shows that the use of pectin results in a more dense mesh of the mixed gel than in the case of agar, but the concentration effect is less obvious.

Table 2

The main rheological characteristics of mixed gels based on Alg₂Ca and agar

Content AlgNa, %	Content Ca ²⁺ , %	Content of agar, %	Deformation			$\gamma_{rev}/\gamma_{tot}$	$\gamma_{irrev}/\gamma_{tot}$	$E_{el} \times 10^3, Pa$
			Total $\gamma_{tot} \times 10^3$	Reverse $\gamma_{rev} \times 10^3$	Irreversible $\gamma_{irrev} \times 10^3$			
2.0	0.4	–	28.0	23.1	5.5	0.82	0.19	115.0
		0.2	24.0	18.8	5.1	0.78	0.21	173.0
		0.4	13.1	8.9	4.2	0.68	0.32	262.0
		0.8	8.8	6.0	2.8	0.68	0.32	441.0

Table 3

Basic rheological characteristics of mixed gels based on Alg₂Ca and pectin

Content AlgNa, %	Content Ca ²⁺ , %	Content of pectin, %	Deformation			$\gamma_{rev}/\gamma_{tot}$	$\gamma_{irrev}/\gamma_{tot}$	$E_{el}\times 10^3, Pa$
			Total $\gamma_{tot}\times 10^3$	Reverse $\gamma_{rev}\times 10^3$	Irreversible $\gamma_{irrev}\times 10^3$			
2.0	0.4	–	28.0	23.1	5.5	0.81	0.19	115.0
		1.0	22.0	16.9	5.0	0.77	0.23	131.0
		2.0	18.6	11.2	7.3	0.60	0.39	140.0

Thus, the percentage of irreversible deformation for the Alg₂Ca gel with 1.0 % of pectin decreased by 4.0 %, whereas it decreased by 14.5 % for 0.8 % of agar. Probably, this effect could be even more prominent in the case of a change in the competition for Ca²⁺ between pectin and AlgNa. For technological reasons, however, the concentration of Ca²⁺ in the system was not changed in the tests. Fig. 7 shows the dependence of the highly elastic modulus of elasticity and the degree of penetration of Alg₂Ca gels on the concentration of low-etherified pectin at a constant concentration of Alg₂Ca.

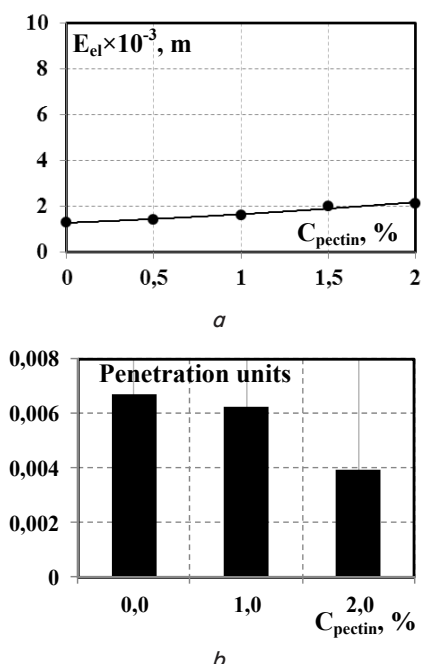


Fig. 7. Dependence of elastic properties of Alg₂Ca gels on the concentration of low-esterified pectin: *a* – modulus of elasticity ($E_{el}\times 10^{-3} m$); *b* – degree of penetration (penetration units)

Fig. 8 shows the dynamics of a relative deformation of Alg₂Ca gels and mixed gels with glycerol with the concentration of AlgNa $C_{AlgNa}=2.0$ % and glycerol in the range of $C=0.5...1.0$ % in the presence of Ca²⁺ (0.4 %).

Table 4 and Fig. 9 show the results of researching the effect of glycerol on the structural and mechanical parameters of Alg₂Ca gels at the concentration of AlgNa $C=2.0$ %, Ca²⁺ $C=0.4$ % and glycerol in the range of $0.5\leq C\leq 1.0$ %. It has been determined that with increasing the content of glycerol in a system with a constant concentration of AlgNa there is a gradual increase in the relative deformation of the mixed gels. The reason for this can be the dilution of the system, which could interfere with the formation of the Alg₂Ca gel.

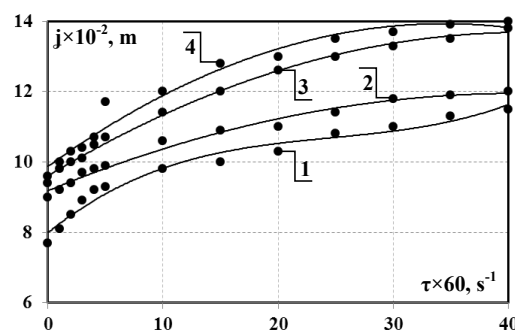


Fig. 8. Alg₂Ca gel creep curves at a temperature of $t=18\pm 2$ °C, the concentration of AlgNa 2.0 %, the concentration of Ca²⁺ 0.4 %, and the concentration of glycerol, %: 1 – 1.0; 2 – 0.75; 3 – 0.5; 4 – reference, respectively

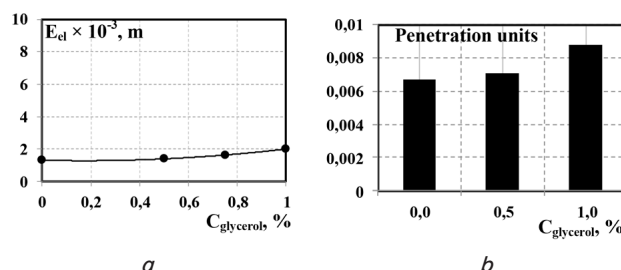


Fig. 9. Dependence of elastic properties of Alg₂Ca gels on the concentration of glycerol: *a* – modulus of elasticity ($E_{el}\times 10^{-3} m$); *b* – degree of penetration (penetration units)

It has been determined that the amount of the yielding capacity of Alg₂Ca is the smallest, and with increasing the content of glycerol, the value decreases practically linearly. The reduction of the elastic modulus is practically linear, which confirms the fact that there is no concentration interaction between Alg₂Ca and glycerol. It can be stated that glycerol does not act as a solvent, but it interferes with the formation of a complete Alg₂Ca gel due to the nature of glycerol. As a result, we have obtained gels that are plastic and unstable in time (Table 4).

Thus, the study has determined the regularities of the effect produced by the composition of the gelators in the three-component systems such as “AlgNa – polysaccharide (agar, low-esterified pectin) – water” and “AlgNa – glycerol – water”. It has been proved that these system compositions facilitate the obtaining of EFSFFP shells with controlled structural and mechanical properties.

On the basis of a set of tests on the influence of thermotropic polysaccharides and glycerol on the properties of the alginate-calcium shell, a technological model of producing EFSFFP was developed. This semifinished product was

obtained by extrusion in the air medium with a modified shell for use in food and culinary products (Fig. 10).

The conducted tests have confirmed the possibility of gel formation with a mixed type of gelation the structural

and mechanical properties of which are subject to a certain technological influence with the provision of consistency characteristics of finished products.

Table 4

The main rheological characteristics of mixed gels based on Alg_2Ca and glycerol

Content AlgNa, %	Content Ca^{2+} , %	Content of glycerol, %	Deformation			$\gamma_{\text{rev}}/\gamma_{\text{tot}}$	$\gamma_{\text{irrev}}/\gamma_{\text{tot}}$	$E_{\text{el}} \times 10^3$, Pa
			Total $\gamma_{\text{tot}} \times 10^3$	Reverse $\gamma_{\text{rev}} \times 10^3$	Irreversible $\gamma_{\text{irrev}} \times 10^3$			
2.0	0.4	–	28.0	23.1	5.5	0.82	0.19	115.0
		0.5	30.3	25.4	5.6	0.84	0.18	106.7
		1.0	35.1	27.5	6.0	0.78	0.21	90.7

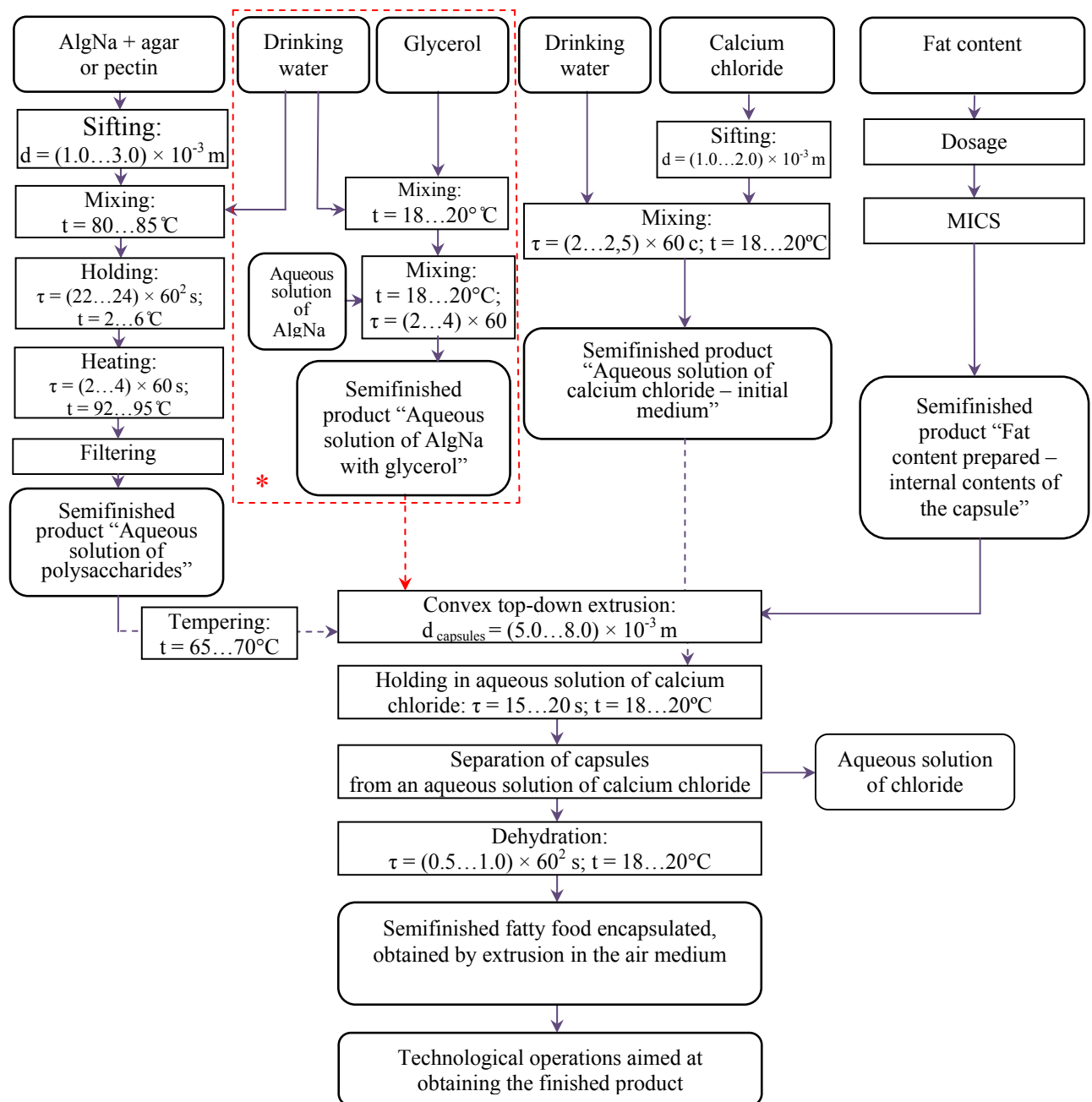


Fig. 10. A technological model of producing an EFSFFP with a modified shell, obtained by extrusion in the air medium:

*— the module under the conditions of using glycerol

6. Discussion of the results of studying the influence of thermotropic polysaccharides and glycerol on the properties of mixtures based on AlgNa

The obtained results show that the use of the principle of mixed gelation significantly influences the structural, mechanical, physical and, as a result, organoleptic parameters of the EFSFFP.

In order to study the possibility of interaction of gelators in a mixed gel, the systems “AlgNa – agar – Ca^{2+} – water” and “AlgNa – low-esterified pectin – Ca^{2+} – water” were tested. In the system “AlgNa – agar – Ca^{2+} – water”, only an aqueous solution of AlgNa interacts with Ca^{2+} , since the sulfated polysaccharide, agar, has no prominent properties for complexation in the presence of Ca^{2+} . It is assumed that meshes of ionotropic Alg_2Ca gel and agar form frame structures of products and exist in it without chemical interaction. However, in the mesh of the “chemical” gel Alg_2Ca it is likely that the “physical” gel of agar appears. In general, the properties of such gels are manifested as the sum of the properties of the gels that are formed by the two gelators with an advantage of the properties of the dominant component. It is known that the aqueous solutions of AlgNa and low-esterified pectin are capable of interacting with ions of divalent metals. Therefore, during the introduction of the Ca^{2+} system, there is a competition for the possibility of interacting with Ca^{2+} and creating an “ Alg_2Ca ” complex and/or a “ Ca^{2+} – low-esterified pectin” system. Under these conditions, there appear two meshes of “chemical” gels for each of the polysaccharides, as well as a complex gel. However, based on the chemical potential of the substances, the aqueous solution of AlgNa is characterized by a much more pronounced interaction with Ca^{2+} than the solution of pectin. As a result, the dominant amount of Ca^{2+} forms chelate compounds with the AlgNa aqueous solution. From this it follows that the mixed gel will exhibit a greater degree of properties of the Alg_2Ca gel, especially as to thermal stability. The results of the study of structural and mechanical parameters in the system “AlgNa – glycerol” confirm the theory of “dilution” of the solvent. The result is an increase in the gel formation time of the system and a controlled process of capsulose formation.

The comparison of the results of the study of the texture modules of the experimental systems confirms the possibility of modifying gels in the direction of density increase for agar and pectin gels under the conditions of introducing an aqueous solution of AlgNa.

The results and conclusions of these tests should be confirmed by parallel studies using other methods. This will help broaden the understanding of the structure formation in

the system of polysaccharides and the simultaneous presence of various mechanisms of gel formation.

Probably, the structural, mechanical and physical properties of alginate-calcium walls of the capsule shell will be influenced by the tactics and tasks that the technological process solves. In this sense, we understand the approaches that underlie the technological process – whether part of the AlgNa aqueous solution in the process flow is replaced by an equivalent concentration of thermotropic polysaccharide, or a new substance is added to the planned concentration of the aqueous AlgNa solution. This approach is very appropriate, since the potential increase in the concentration of thermoionotropic gelators in the system can lead to a thickening of the mesh of the mixed gel, thus altering the structural and mechanical properties of the capsule shell. Such a pattern will manifest itself at all concentrations of the experimental polysaccharides.

According to the results of the research, it can be concluded that the characteristic of the gel is organized by mixed gel formation; its elastic-plastic and technological properties depend on many factors. This may be the choice and concentration of the polysaccharide, the properties of the solvent, the extent of conversion of AlgNa into Alg_2Ca , the concentration ratio of the components and the temperature of the external environment, which determines the mobility of hydrogen bonds. It is evident that mixed gelation makes it possible to affect the organoleptic parameters and the physiological value of the EFSFFP significantly. In line with the structural and mechanical characteristics, it also includes the permeability for ferments during homeostasis and the ability to hold moisture, thus providing the organoleptic characteristics of the finished product.

7. Conclusions

1. It has been determined that the use of EFSFFP shells of agar and low-esterified pectin in the mixture results in a linear increase in the elastic properties of the gel shell in proportion to the concentration of the injected polysaccharide to the constant concentration of Alg_2Ca . The introduction of glycerol leads to a monotonous decline in the modulus of elasticity of gel capsules.

2. The principal possibility of controlling the structural, mechanical and organoleptic properties of EFSFFP shells has been proven. The result is an increase in the coefficient of permeability of the capsule shells and the correction of the moisture-retaining and moisturizing ability of the encapsulated systems. This helps expand the range of using new products in the technology of encapsulation of fats and food products.

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