

В рамках проведених досліджень розроблено технологічні принципи виробництва гранульованих наповнювачів. Дослідження здійснювали на модельних системах (гранулах), що дозволило визначити умови утворення альгінат-кальцієвих комплексів. Визначено, що основним принципом одержання гранул є співвідношення мануринових та гулуринових залишків у складі альгінату натрію, яке для реалізації процесу гранулоутворення має складати $\chi=0,4..0,6$. Доведено, що вміст G-блоків у складі альгінату натрію повинен бути у межах 20...25 %, що за вмісту іонного кальцію в межах 80–120 мг % забезпечує утворення стійких альгінат-кальцієвих комплексів. Визначено, що зростання модуля пружності структурованих систем залежить від концентрації альгінату натрію, умов реалізації його сорбційних властивостей відносно іонів кальцію та кількісного вмісту заряджених частинок.

Доведено зниження сорбційної ємності альгінату натрію за зниження рН, оскільки має місце обмін іонів натрію на іони Гідрогену, тобто утворення альгінових кислот (HAlg), які мають низьку здатність до дисоціації та іонообміну. Експериментально підтверджено, що використання сировини з низьким значенням рН в технології гранульованих наповнювачів на основі альгінату натрію не тільки буде зменшувати модуль пружності гранул, а й сприятиме втраті прозорості систем.

Досліджено вплив цукрових сиротів, рН середовища та термообробки на модуль пружності та зміну маси гранульованих наповнювачів. Встановлено, що за впливу вищезначених чинників має місце збільшення модуля пружності гранульованих наповнювачів та зменшення їх маси внаслідок часткового виділення вологи. З урахуванням визначених технологічних принципів розроблено модель технологічної системи виробництва гранульованих наповнювачів. Означено особливості ведення технологічного процесу за умови використання молочної сировини, алкогільвміщуючої сировини, сировини з низьким значенням рН

Ключові слова: гранульовані наповнювачі, альгінат натрію, іонний кальцій, альгінат-кальцієвий комплекс, іотропне гелеутворення

UDC 66.022.32-026.772:544.77.022.822

DOI: 10.15587/1729-4061.2020.200098

DEVISING THE TECHNOLOGICAL PRINCIPLES FOR MAKING A GRANULATED FILLER OBTAINED THROUGH IONOTROPIC GELATION

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Received date 02.02.2020

Accepted date 27.03.2020

Published date 24.04.2020

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1. Introduction

Under current conditions, most enterprises in the food and restaurant industries seek to expand their presence on food markets. One of the ways to expand the sales market is to diversify production whose significant component is managing the assortment of foods.

At present, the range of food products is characterized by wide use of fillers (stuffing) – fruit and berry [1, 2], vegetable, dairy [3], chocolate [4], nut [5], cereals. Their application in dairy, confectionery, bakery, and other food industries, in addition to a wider range [6], makes it possible to create the new consumer properties of products [7], reflecting the preferences of the end-user, by correcting the

nutritional value [8], enrichment with vitamins, macro- and microelements and food fibers [9], by adjusting energy value, that is, to form the basic identifiers of the consumer socialization of products. It should be noted that the use of fillers under a condition of the implementation of typical technological processes for making food products can increase the mobility of enterprises, increase the share of profits at the unchanged and/or larger number of manufactured products.

The production of granulated fillers is increasingly popular. This relates to that the granulation, first of all, provides an opportunity to create a variety of physical and geometric forms of fillers, which allows mixing them with different food systems (liquid, viscous, solid, etc.) without any difficulties. However, currently, the well-known technologies for making

granulated fillers come down to the formation of a product from a wet formulation mixture followed by its drying. Thus, for example, chocolate drops or rice balls are made. At the same time, manufacturing granulated fillers of gel-like texture is rather limited due to the lack of generalized scientific approaches, as well as the necessary equipment for the industrial implementation of such technological solutions.

Therefore, it is a timely and relevant task to devise the technological principles for making granulated fillers, which are thermally stable, have a spherical shape of granules of different diameters, various textures – from soft and elastic to dense and crispy. At the same time, the development of such a unique approach would make it possible to effectively improve conventional technologies in order to meet versatile taste preferences by modern consumers.

2. Literature review and problem statement

In recent years, a series of innovations have been developed and introduced into the technology of fillings, which imply the application of modern food technologies: sublimation, drying, freezing, structuring, etc. Their implementation helps obtain fillers in the form of heat-resistant fillings, powders, pieces of dehydrated fruits; fillers in the form of structured capsules and granules [10–13] are now common. Given the requirements for fillers, the most demanded ones are thermally stable. The stability of fillers properties under the influence of technological factors – temperature, pH, mechanical action – allow them to be used in the culinary and confectionery products, which undergo heat treatment at temperatures from 80 °C to 250 °C (frying, baking), as well as freezing and microwave treatment. Thus, paper [14] defines the requirements and substantiates the technological parameters for making heat-resistant fillers based on fruit and berry raw materials – dispersity, the content and ratio of structure-forming components (pectins, alginates, carrageenan), stabilizers of consistency, and other ingredients. When the stabilization systems are used in the amount of 1.2...1.5 %, the fillers are thermally stable, do not flow out of the dough shells, retain plasticity; however, during storage, they have a tendency to retrograde, which proceeds with such consequences as compaction of the gel, pressing out the moisture.

One of the ways to resolve the specified issue is to introduce hydrocolloids that can retain the moisture in the system and prevent gels sealing processes. Thus, the authors of [15] proved the expediency of using a composition containing xanthan gum (XG), Arabian gum (AG), guar gum (GG), pectin (PC), and carboxymethylcellulose (CMC) at a concentration of 0.2 %, 0.4 %, 0.6 %, 0.8 %, and 1.0 %, respectively, as part of the thermostable fillings made from mango. By optimizing the composition, the authors substantiated its rational content in the fillings – to 1.0 %. They studied the influence of moisture content, soluble substances, pH, on the viscosity and thermostability of mango fillings and substantiated the technological parameters for their production.

A possibility of using syrups with a high content of solids, thickeners and lyophilized strawberry, passion fruit, and orange peel was investigated in work [16]. The stability and shelf life of the fillers were examined by defining the structural and mechanical parameters – viscosity, shear stress, plasticity. It was experimentally established that the presence

of sucrose provides stable viscosity and shear stress within 90 storage days. Recommendations on the use of fillers in the composition of biscuits, rolls, desserts were devised.

In addition, one of the problematic issues related to the existing technology of fillers is the stability of their qualitative indicators under the influence of temperature.

The authors of [17] proposed to solve this task by using a binary combination of polysaccharides for thermo-resistant milk-containing fillings. They determined the rational parameters for obtaining composite mixtures of polysaccharides with synergetic properties, which are used for adjusting the structural and mechanical properties of food systems. It was established that it is rational to use a mixture of xanthan gum and Tara gum in the ratio of 60:40.

In addition, a study [18] established and optimized the impact of technological factors on the formation of the structure of a thermostable filling based on pumpkin hydrolyzed puree. In order to create a pumpkin topping with the thermo-reversible and thixotropic properties, an additional structure-forming agent was used – the low-esterified amidated pectin APC 210C with a degree of esterification of 30 %. It was discovered that the optimal content of this type of pectin is 0.8 %. To reinforce the binding properties, the developers used calcium citrate in an amount of 0.1 % at the mass fraction of salt of 70 %. The authors devised a formulation for the pumpkin filling, which contains an increased amount of pectin, plant-based fiber, β -carotene, and has a reduced caloric content.

By summarizing the data given above, it should be noted that the result of all specified technologies is the fillers representing a homogeneous viscous, plastic mass. Such rheological properties cause certain difficulties during its dosing and forming the resulting products that contain it. This necessitates the search and creation of new technological procedures for obtaining fillers with a stronger and more elastic frame structure, for example, the structured ones.

It is promising now to produce the encapsulated and granulated fillers obtained through ionotropic gelation [19, 20]. Thus, there is a scientifically justified process of obtaining granulated fillers, based on the principle of ionotropic gelation. It was found that the required textured and geometric properties of granulated products are provided by the use of AlgNa, agar, j- carrageenan, and CaCl₂ during the drip extrusion. The development of the technology helped determine the following parameters, under which the chemical processes and physical-chemical conversion are intensified: the dispersity of pumpkin and carrot puree, which should be in the range $(0.5...0.7) \times 10^{-5}$ m, and the rational content of the liquid base, 20...30 % by weight. It was found that a mass fraction of the puree in the amount of 52.0...54.0 % by weight allows the extrusion to be performed most effectively and helps obtain the highest quality extrusion products, with long shelf life, organoleptically attractive, of high strength and elasticity, etc. The devised granulated fillers can be recommended as semi-finished products to improve the quality and nutritional value of sweet meals. The limiting factor of the proposed technology is the use of thermal influence at temperatures 150...200 °C. This is due to the nature of the gel (thermotropic), obtained on the basis of agar and carrageenan. The application of sodium alginate could partially stabilize the structural and mechanical properties of granulated fillers in the temperature range 50...150 °C. However, at high temperatures, the hybrid gel mesh would melt (due to the destruction of the thermotropic gel), which would be

accompanied by significant softening of the fillers' texture, with their subsequent deformation.

Paper [21] scientifically justified and predicted the patterns in the encapsulation of sauces based on tomato products in order to obtain fillers for salads, sausage products, pate. The rational parameters of the technological process were determined: a sodium alginate concentration in the forming solution of 1.5...1.7 %; the content of calcium chloride in a sauce is 0.5 %; the content of NaCMC, treated with the US-wave dispersion, is 1.6 %. It was established that the selected concentrations ensure the formation of capsules at $K_f=1$ and diameter (d) of $(2...3) \cdot 10^{-3} \leq d \leq 8 \cdot 10^{-3}$ m. The authors substantiated the expediency of introducing to the composition of fillings 6...8 % of starch in a non-gelatinized state, which ensures a viscosity of the sauce inside the capsules of 6...10 Pa·s after their heat treatment at a temperature of 82...85 °C for (43...47)·60 s. It should be noted that the encapsulated fillers are more thermally stable compared to granulated; the cited paper, however, states that the membrane of the capsules is rather sensitive to the sodium ions that are part of kitchen salt. In the presence of free ions of Na^+ , the shell of the capsules becomes thinner and more sensitive to a mechanical impact.

There is a known technique for making a granulated product by extruding a formulation mixture to the forming medium, which is fat-free skimmed milk [22, 23]. The mixture contains a solution of sodium alginate, 0.5...3.0 % by weight; the ratio of the mixture to the forming medium is (1...5):10. At the specified parameters (sorption temperature, 2...20 °C, milk pH is 5.0...5.5, the character of sorption temperature is dynamic), the heat-stable granules are formed, which is a result of implementing the chemical potential of milk's calcium ions in the system of alginate gel. The resulting granules can be used as the filling, decoration, mince in the culinary and/or confectionery products. However, a given technological procedure can be effectively used only for the decalcification of dairy raw materials, and the resulting granulated products are positioned only as the related products. In this case, the introduction to the formulation of fruit and vegetable raw materials is not appropriate, because there could occur the diffusion processes at which the coloring substances of plant-derived raw materials would diffuse from the granules into the forming medium (milk), giving it undesirable coloration. In addition, the use of dairy raw materials leads to significant difficulties in the course of the technological process due to the need for thorough control of microbiological indicators of the medium and a simultaneous increase in the cost of the end product.

It should be noted that the current global experience in the field of structured fillers production is wide enough. However, it focuses on specific targeted technologies using a limited range of a raw material base. There are not enough systemic studies aimed at defining and generalizing the technological principles for making granulated fillers obtained from ionotropic gelation. The model of the technological process requires clarifications and explanations. One should also pay attention to the need to devise an expanded range of recommendations for the use of granulated products in the culinary and confectionery products.

All this calls for the systematization of knowledge and approaches to devising the technological principles for making granulated fillers, the further use of which as semi-finished products with a high degree of readiness would make it possible to obtain foods based on the raw materials of both plant and animal origin with fundamentally new and useful

properties, the predefined nutritional value, and high-quality indicators over long shelf life.

3. The aim and objectives of the study

The aim of this study is to devise the technological principles for making granulated fillers obtained through the ionotropic gelation.

To accomplish the aim, the following tasks have been set:

- to study theoretically and experimentally the conditions to form alginate-calcium complexes;
- to define the rational parameters of granule formation based on sodium alginate and calcium ions;
- to build a model of the technological system for making granulated fillers;
- to investigate the influence of technological factors on the organoleptic and structural-mechanical properties of granulated fillers.

4. Objects and methods to study granules and granulated fillers

Our study objects are:

- sodium alginate (AlgNa) FD-157 with a value of $\chi = 0.58$ (manufactured by Danisco, Denmark; χ is the ratio of guluronic and mannuronic acids);
- granules (model systems "AlgNa–Ca"), made on the basis of AlgNa solutions at a concentration of 1.0...2.0 % and a CaCl_2 solution at a concentration of Ca^{2+} of 7.0...120.0 mg %;
- granulated fillers.

We obtained the granules (as model systems) and granulated fillers by a drip injection of the formulation mixture on the basis of sodium alginate to the solution of calcium chloride, followed by the exposure of the granules to a calcium-type solution for (0.5 ...60)·60 s with subsequent decanting and washing the granules in running water at a temperature of 18–20 °C.

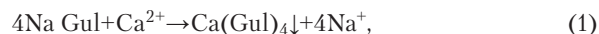
The methods for studying the physical-chemical, functional-technological, and structural-mechanical properties of the model granulated products are described in detail in paper [24].

Our experimental study was conducted at the laboratory of rheological research at Kharkiv State University of Food and Trade (Ukraine).

5. Results of studying the patterns in the formation of granules based on sodium alginate

5.1. Theoretical and experimental substantiation of the conditions for alginate-calcium complex formation

It is commonly known that the introduction, under a dosed (drip) mode, of an aqueous solution of sodium alginate to an environment containing calcium ions can make it possible to obtain spherical products in the form of granules [25–27]. The shape formation (granulation) as a result of the reaction is described by the following equations:



or



since the thermal effect of the exothermic reaction (1) exceeds the enthalpy of reaction (2) by 330 kJ/mol and depends on the potential of the system, it becomes possible, given the equation by Arrhenius, to determine the constant rate of the reactions.

An important factor for the progress of technological processes under actual conditions is the sufficient amount of reacting substances. Thus, during granulation, calcium ions not only implement the function of blocking electrolytes but also act as a “construction” material. That is, the complex compounds of calcium with the remains of guluronic acids (CaGul₄) bind to the analog block of another chain of the polymer molecule and form a frame spatial structure. However, the progress of this process is only possible at a sufficient amount of calcium ions. In addition, the crosslinking also involves those regions that contain sodium, that is, the mannuronic and guluronic residues.

The formation of crosslinked regions of sodium alginate significantly decreases the number of hydrogen bonds, which provides the affinity of the latter with the solvent molecules. At a high content of calcium ions, the frame and strength of the system “Alg-Ca-Na” would grow rapidly. That could lead to a spatial arrangement of macromolecules chains. At a certain concentration of calcium ions under the reasonable concentration of sodium alginate (provided its content includes at least 20...25 % of G-blocks), the interaction between a polymeric chain of sodium alginate and a solvent becomes an energetically unfavorable process. At the same time, due to the increase in the number of crosslinking points and blocks, at which hydrogen bonds cannot be formed, the alginate chains close and form the energetically favorable spatial structures, which form the granules.

In the first phases, a granule is mechanically unstable. Provided that there is a gradient of concentrations in the receiving environment in terms of calcium content relative to the internal content, that is, there is a concentration imbalance, there is the diffusion of calcium ions inside the granules. This is a technological condition for obtaining granulated products.

Gelation, as a result of ion-exchange reaction, described by equation (2), would lead to the formation of granules, which can be assessed in an actual process based on the growth rates of the gel elasticity module. The intensity of an AlgNa solution transformation to the system “AlgNa-Ca” depends on many factors, and especially on:

- the ratio of guluronic to mannuronic acids $\left(\chi = \frac{C_{GA}}{C_{MA}}\right)$

in the composition of sodium alginate, which is $\chi = 0.4...0.6$ to enable the process of gelation;

- the mass fraction of calcium ions;
- the procedure for introducing the reacting components (the introduction of sodium alginate to a solution of calcium-containing salts, or vice versa);
- the duration of ion exchange and the magnitude of mass exchange.

To substantiate the technological parameters for making granules, the model systems were used to study the sorption capacity of AlgNa (Fig. 1), the regularities of sol-gel transitions with the formation of a physical interface, the detachment efforts (Table 1). This allowed us to simulate actual interactions in the case of using food raw materials with different pH values.

It was established experimentally that the kinetics of calcium ion sorption depends on the concentration of sodium

alginate, pH of the medium, and the duration of sorption. Thus, increasing the concentration of AlgNa in a solution from 1.0 % to 2.0 % leads to an increase in the absorbed Ca²⁺: at pH 7.0±0.1 – from 10.2 % to 15.3 %, at pH 5.5±0.1 – from 7.2 % to 13.0 %, at pH 4.0±0.1 – from 8.1 % to 11.6 %. Over the first (7–15)-60 s, the process of sorption is highly dynamic, it continues to slow down and stop.

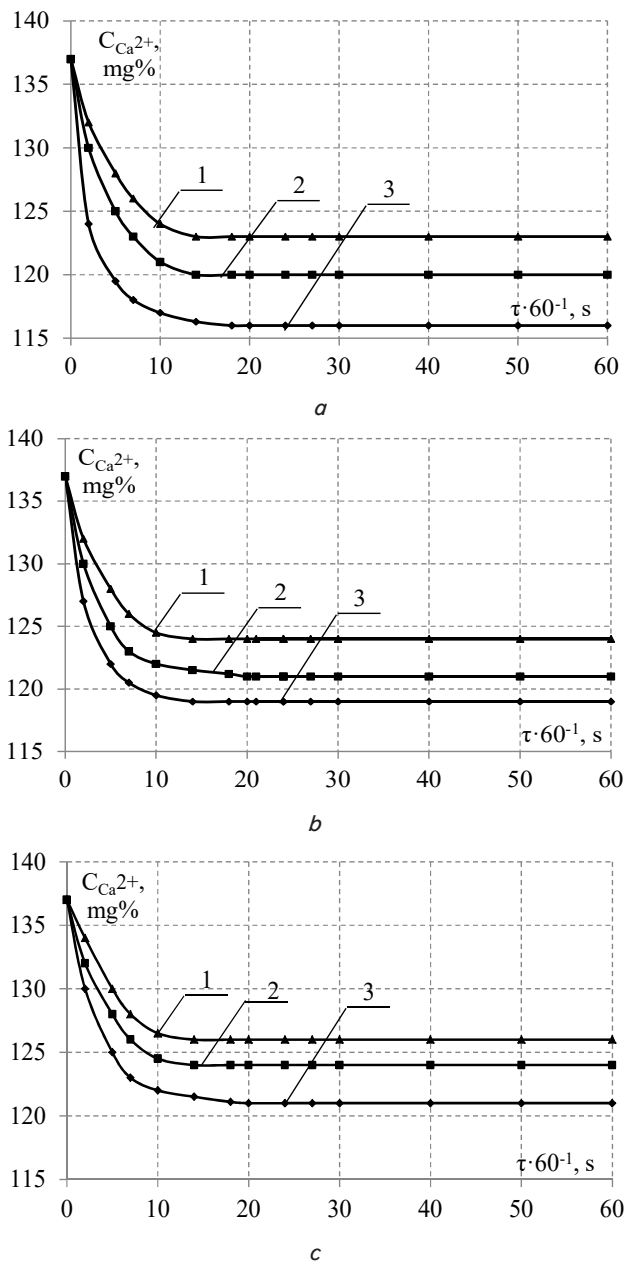


Fig. 1. The kinetics of sorption of Ca²⁺ from a CaCl₂ solution at AlgNa concentration (1, 2, 3 – 1.0; 1.5; 2.0 % respectively) and different pH ($t=20.0\pm 0.5$ °C): a – pH 7.0±0.1; b – pH 5.5±0.1; c – pH 4.0±0.1

In the first stage of sorption, a high rate of Ca²⁺ binding is observed, which, along with other factors, depends on the concentration of AlgNa. The amount of Ca²⁺, which is absorbed by a 1.0 %, 1.5 %, and 2.0 % solution of AlgNa after 10-60 s, is, respectively, 9.4±0.1 %, 11.6±0.1 %, and 14.5±0.1 % of the original content (at pH 7.0±0.1). This indicates a high sorption ability of sodium alginate. The second stage, which characterizes the system in terms of sorption capacity, is char-

acterized by the presence of a plateau on the sorption curve. An analysis of the data shown in Fig. 1 allows us to assert that the magnitude of the system's pH affects the rate of sorption capacity. Thus, decreasing the pH values from 7.0 ± 0.1 to 4.0 ± 0.1 is accompanied by a decrease in the sorption capacity. The result of the change in pH from 7.0 ± 0.1 to 5.5 ± 0.1 is a decrease in the amount of calcium that is absorbed, by 7.0 %, and in pH to 4.0 ± 0.1 – by 15.0 %, regardless of the concentration of reacting substances. This effect is likely due to that there is a partial transition of sodium alginate into the HAlg state with a low capability to dissociation and ion exchange.

Thus, the main condition for the formation of alginate calcium complexes is the implementation of sorption processes between calcium ions and sodium alginate. The drivers of such processes are the residues of guluronic acids in the composition of sodium alginate, that is, its reactivity. Also important is to create appropriate conditions for the activation of sodium alginate, that is, maintaining the pH of the system not less than 5.0.

5.2. Determining the rational parameters for granule formation under conditions for implementing a reaction of ionotropic gelation

The binding of calcium ions by sodium alginate is accompanied by a change in the structural and mechanical properties of the systems. We have established an initial rapid increase in viscosity, followed by the further formation of elastic properties of the structured systems "AlgNa–Ca". Thus, in the range of concentrations of Ca^{2+} from 7 to 40 mg %, there is a rapid increase in the module of instantaneous elasticity (from $(0.5 \pm 0.01) \cdot 10^3$ Pa to $(10.7 \pm 0.1) \cdot 10^3$ Pa), then there is a gradual growth in it (Table 1). It is important to note that an increase in the elasticity module of the structured systems depends on the mass fraction of calcium ions and the concentration of sodium alginate, which is the result of its sorption properties. Data in Fig. 2 clearly indicate that in the interval of calcium ions concentrations of 40...110 mg % the instantaneous elasticity module grows by 1.10; 1.35; and 1.40 times, respectively, for sodium alginate in a concentration of 1.0; 1.5; and 2.0 %.

The granules that were formed must be separated from the forming medium. On the one hand, this is a mandatory technology operation, on the other hand, the removal of granules under the specified technological parameters would ensure the stability of the organoleptic and physical-chemical quality indicators. This defines the expediency of investigating an effort of the detachment of the structured systems from the forming environment (Table 1).

An effort of the detachment of the "AlgNa–Ca" granules from distilled water depends on the stage of a structure formation, that is, on the ratio of the formed CaGul_4 to AlgNa, which did not enter a chemical reaction with Ca^{2+} under a condition of their shortage. The systems that are more concentrated in terms of the AlgNa content show a higher affinity to distilled water, which complicates their separation.

The effort of the detachment of the "AlgNa–Ca" granules from the solutions of calcium chloride at a Ca^{2+} concentration of 70.0...120.0 mg % in all cases is relatively low. Thus, at an AlgNa concentration of 1.0 % and the specified content of Ca^{2+} , the effort of the detachment of the "AlgNa–Ca" systems from a solution of calcium chloride decreases from 30.0 ± 0.5 Pa to 20.0 ± 0.5 Pa. Our study makes it possible to predict the effective separation of the "AlgNa–Ca" granules from the forming medium.

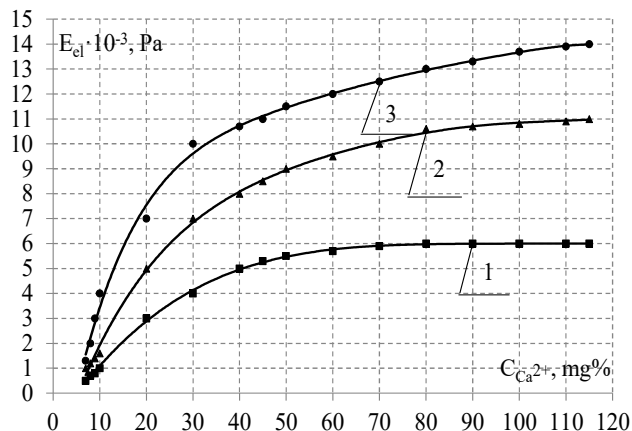
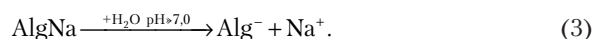


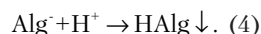
Fig. 2. Dependence of the module of instantaneous elasticity of the model systems "AlgNa–Ca" on the concentration of AlgNa, % ($t=20.0 \pm 0.5$ °C): 1, 2, 3 – 1.0; 1.5; 2.0, respectively

The effective course of a cooperative-type reaction with the formation of granules is possible under the pH values close to 7.0, which ensures an almost absolute solubility of sodium alginate, that is



The kinetics of the AlgNa process of gelation in the presence of Ca^{2+} would depend on the conditions of its solubility in the acidic environment. This indicator must be evaluated because the acidity of the system would determine the structure of the gel based on sodium alginate and the ability to run a reaction between Ca^{2+} and Alg^- . At the reduced pH, there is a buffer capacity that promotes the removal of acids from the structure of sodium alginate to a partially dehydrated gel. Under these conditions, Ca^{2+} would be bound by the Alg^- anions in proportion to their concentration in the solution.

The chemical equilibrium of the reaction would shift to the right, that is, towards the formation of an Alg_2Ca gel, with the prevailing CaGul_4 complexes. But the mass fraction of such a gel would be proportional to the concentration of acidic residues of alginate acids, which is determined by a binding degree of the carboxylic groups COO^- with the H^+ ions contained in the AlgNa system. That is, from a technological point of view, control over the pH of the medium is important because at high acidity the acidic gel could form (scheme 4):



We have estimated the impact of $[\text{H}^+]$ on the formation of $\text{Alg}_2\text{Ca} \downarrow$ at the known concentrations of Alg^- and Ca^{2+} . Fig. 3 shows the dependence of the instantaneous module of elasticity of the granules ($C_{\text{AlgNa}}=1.5$ %; $C_{\text{CaCl}_2}=0.8$ %) on the pH value.

One can see that a decrease in the pH of the system from 7.0 ± 0.1 to 4.0 ± 0.1 reduces the value of an elasticity module by 1.62 times – from $15.9 \cdot 10^3$ to $9.8 \cdot 10^3$ Pa. The acidity of the system significantly affects both the process of granulation and the module of elasticity of the granules. In the interval of pH of 4.0...5.0 one visually registers the blurred gels, which is a sign of the formation of "acidic" gels containing mostly the amount of HAlg \downarrow . To investigate this phenomenon, we examined the light diffusion of sodium alginate solutions depending on concentration at a pH of 4.0 ± 0.1 (Fig. 4).

Table 1

Characteristics of granules obtained through ionotropic gelation

System characteristic	Concentration		Structural -mechanical properties		Detachment effort (Pa) from calcium chloride solutions that contain Ca ²⁺ , mg %				
	AlgNa, %	Ca ²⁺ , mg %	η, Pa·s	E _{el} 10 ³ , Pa	0	10.0	45.0	80.0	120.0
AlgNa solution	1.0	–	0.12±0.01	–	–	–	–	–	–
Model system «AlgNa–Ca»	1.0	7.0±0.1	–	0.8±0.01	30±1	27±1	23±1	21±1	20±1
Model system «AlgNa–Ca»	1.0	45.0±0.1	–	5.1±0.01	26±1	24±1	23±1	21±1	20±1
Model system «AlgNa–Ca»	1.0	80.0±0.1	–	6.0±0.01	24±1	22±1	21±1	21±1	20±1
Model system «AlgNa–Ca»	1.0	115.0±0.1	–	7.1±0.01	22±1	21±1	20±1	20±1	20±1
AlgNa solution	1.5	–	0.42±0.01	–	–	–	–	–	–
Model system «AlgNa–Ca»	1.5	10.0±0.1	–	0.9±0.01	38±1	34±1	32±1	30±1	29±1
Model system «AlgNa–Ca»	1.5	45.0±0.1	–	8.5±0.01	32±1	28±1	27±1	26±1	25±1
Model system «AlgNa–Ca»	1.5	80.0±0.1	–	10.6±0.01	27±1	25±1	24±1	23±1	22±1
Model system «AlgNa–Ca»	1.5	120.0±0.1	–	11.0±0.01	25±1	24±1	23±1	23±1	23±1
AlgNa solution	2.0	–	0.74±0.01	–	–	–	–	–	–
Model system «AlgNa–Ca»	2.0	10.0±0.1	–	1.0±0.01	46±1	42±1	40±1	41±1	38±1
Model system «AlgNa–Ca»	2.0	45.0±0.1	–	11.0±0.01	34±1	32±1	32±1	30±1	30±1
Model system «AlgNa–Ca»	2.0	80.0±0.1	–	13.0±0.01	30±1	29±1	29±1	28±1	28±1
Model system «AlgNa–Ca»	2.0	120.0±0.1	–	14.0±0.01	28±1	27±1	27±1	27±1	27±1

Note: Dark color denotes the indicators at which the detachment of granules from the surface of a CaCl₂ solution occurs without obstruction

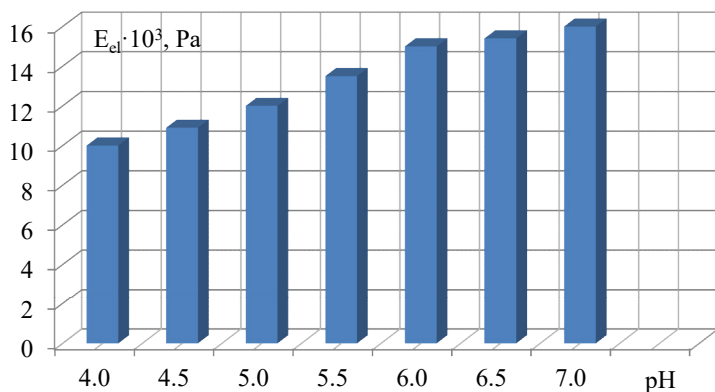


Fig. 3. Dependence of the instantaneous module of elasticity of the granules (C_{AlgNa}=1.5 %; C_{CaCl₂}=0.8 %) on the pH value

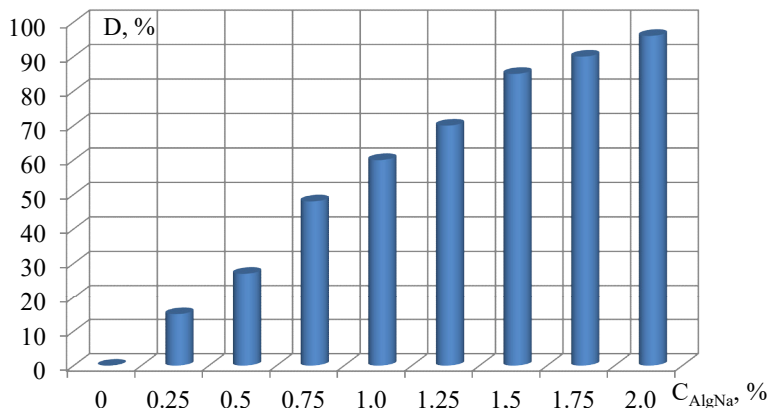


Fig. 4. Dependence of light diffusion of the sodium alginate solutions on its concentration at pH 4.0±0.1

It was determined that in the studied range of sodium alginate concentrations there is a polymer aggregation. That is, an increase in the concentration of sodium alginate in the

solution leads not only to the decrease in the number of aggregation centers but also changes their dimensional characteristics with the emergence of the effect of a polymer “super-aggregation” at the center of its localization.

Fig. 5 shows the graphic dependences of the amount of the formed acidic gel HAlg↓ on pH at a concentration of sodium alginate of 1.0 %, 1.5 %, 2.0 %.

It was found experimentally that the solutions of sodium alginate at different concentrations in the range of pH 2...7 have a different magnitude of light diffusion, confirming the degrading effect of pH on their properties. The curves' shapes indicate that the formation of HAlg↓ occurs at a different, characteristic of a given concentration, rate, which was determined based on the tg value for an inclination angle of the tangent to the curve. It is evident that the use of low pH raw materials in the technology of granulated fillers based on sodium alginate would not only affect the module elasticity of the granules (by reducing) but also contribute to the occurrence of turbidity. This should be taken into account when devising the technology and a formulation of fillers and be used in the composition of granules, where the reduction of transparency would not be perceived as a deterioration of quality indicators.

The obtained results allow us to formulate the rational parameters for the formation of granules based on sodium alginate and ionic calcium:

- firstly, the content of sodium alginate in a formulation mixture should be about 1.0...1.5 %;
- the concentration of calcium ions in a solution for structuring can vary in the interval 10.0–120,0 mg %;
- for the effective implementation of a gelation process, it is necessary to ensure the pH of the system not less than 5.0.

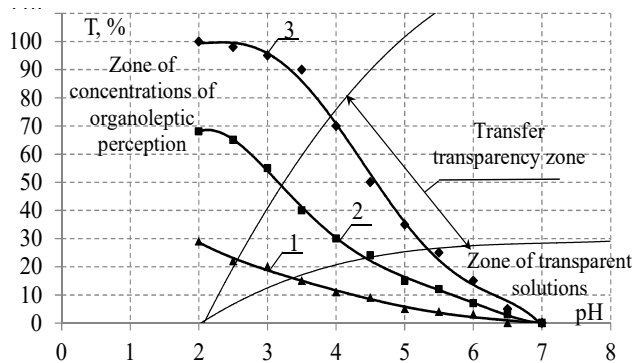


Fig. 5. Dependence of light diffusion of the HAAlg↓ gel on pH at AlgNa concentration, %: 1, 2, 3 – 1.0; 1.5; 2.0 %

However, a simultaneous variation of the defined parameters makes it possible to obtain granulated fillers with different qualitative indicators depending on the technological requirements.

5. 3. Constructing a model of the technological system for making granulated fillers

Based on our research, one can note that the chemical interaction between sodium alginate and calcium ions could be used in the technology of granulated products, which could be used as fillers, toppings for various food products. It should be noted that at the defined rational concentrations of sodium alginate, there will always occur an increased elasticity of the obtained granules. This provides a possibility to introduce additional formulation components to the system, which would determine a product range and adjust the structural-mechanical and organoleptic properties of granulated fillers (Fig. 6).

Based on data in Fig. 6, it can be argued that the range of formulation components is wide enough, represented by the raw materials of both animal and plant origin. However, the use of certain additional formulation components would determine the need to adjust the technological parameters for obtaining granulated fillers.

Thus, the use of fruit and berry raw materials, characterized by low pH value, would determine the need to increase the concentration of reacting substances, in particular AlgNa, because at low pH values the reaction of gelation would slow down while the elasticity of the obtained granulated products would reduce (Fig. 2).

The use of dairy raw materials in the composition of granulated fillers would help improve the rate of gelation. This is evident because the milk pH is 6.8, which is optimal for dissolving and activating sodium alginate. In addition, dairy products would serve an additional source of calcium ions, which dictates the need to reduce the concentration of calcium chloride in the receiving environment.

The finely-dispersed pastes (meat, fish, vegetables, and others) in the composition of granulated fillers would perform the role of “baking powders”, affecting the rate of an ion exchange reaction and the module of elasticity of the resulting products.

The use of sugars with a highly concentrated content (honey, maple syrup, toppings), or alcohol-containing (liqueur, wine, rum) formulation components in the composition of granulated fillers would also require a slight adjustment of the technological process parameters, specifically the mass fraction of reacting substances and the duration of ionotropic gelation.

Therefore, when implementing the specified technological principles for making granulated fillers, each particular case requires technological testing. A model of the technological system for making granulated fillers is shown in Fig. 7.

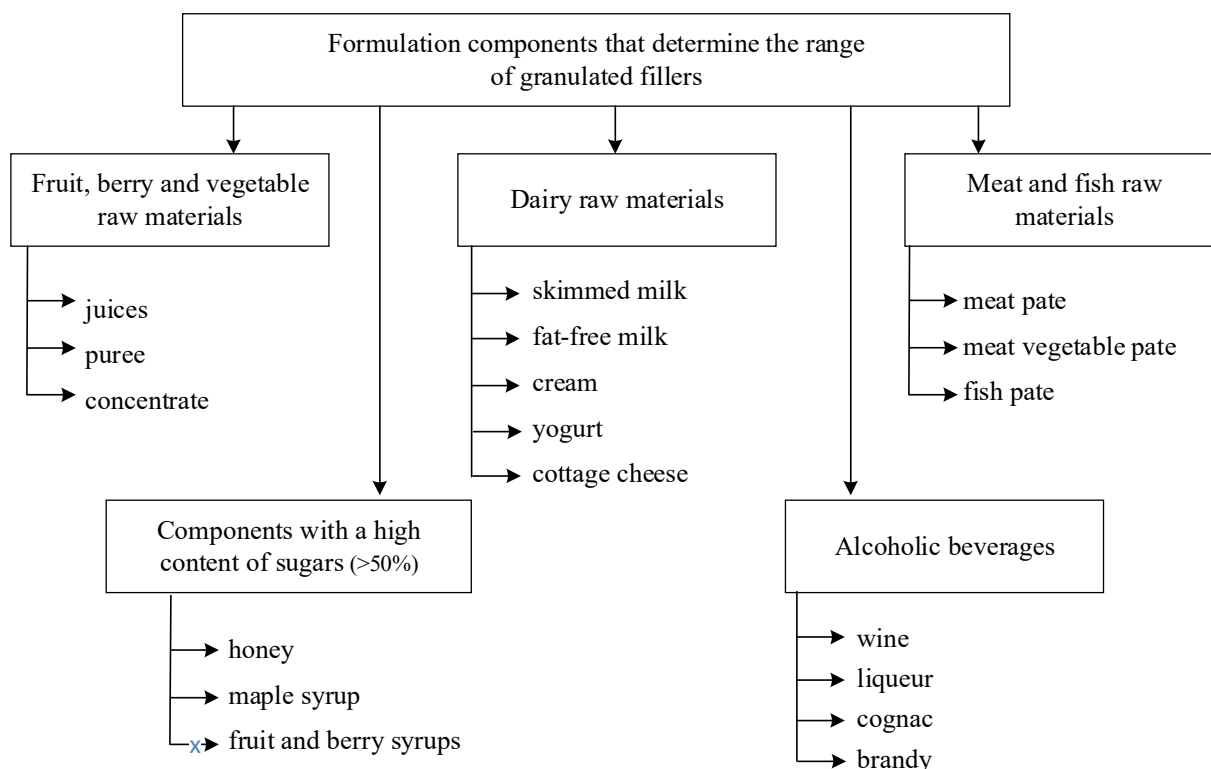


Fig. 6. Formulation components that determine the range of granulated fillers

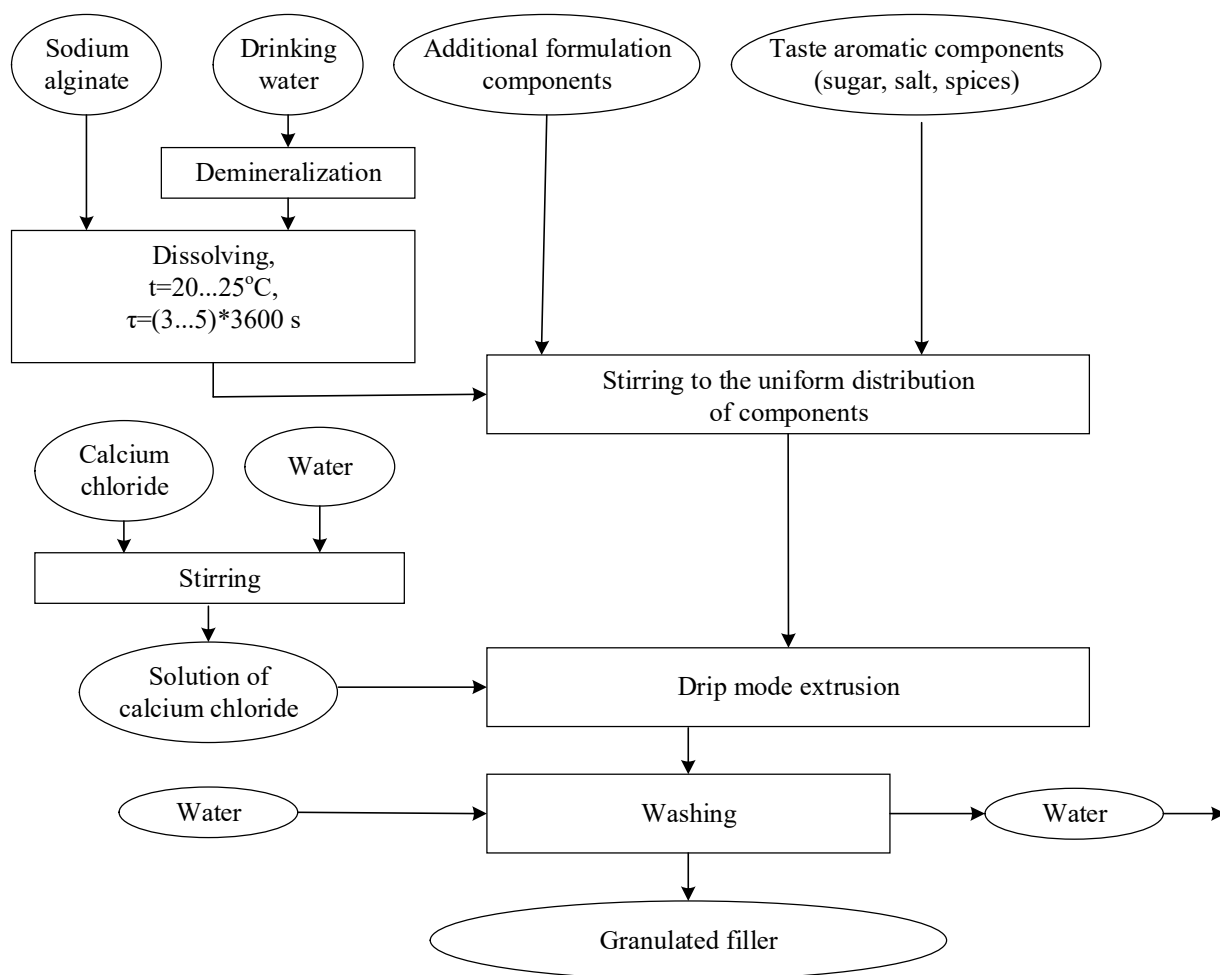


Fig. 7. A model of the technological system for making granulated fillers

According to the devised model, the technological process of granulated fillers production is carried out in the following order. In the first stage, a solution of sodium alginate is prepared. To this end, one dissolves in preliminary prepared water (by demineralization) the necessary amount of sodium alginate at 20...25 °C. The resulting solution is aged for 3...5 hours for the complete dissolution of the polymer.

At the next stage, one adds to the resulting solution the formulation components, which determine the range of finished products (fruit puree, vegetable puree, finely dispersed meat, fish masses, sugar, and others) and taste aromatic components (if necessary), followed by stirring to the uniform distribution of the components.

A formulation mixture is injected (extruded) under a drip mode; the formed granules are aged for (2...5)·60 s in a solution of calcium chloride at 0.9...1.1 % concentration). The treatment duration would be determined by the diameter of the granules ((1.5...10)·10³ m, the concentration of sodium alginate (1...2 %), as well as the qualitative and quantitative composition of the formulation components. The formed granules are removed from the solution of calcium chloride and washed in running water to remove calcium chloride residues from the surface of the product. Under conditions of the rational ratio of sodium alginate to chloride calcium, it is possible to obtain granulated fillers with the predefined structural-mechanical and organoleptic properties.

5. 4. Determining the impact of technological factors on the formation of the organoleptic and structural-mechanical properties of granulated fillers

An expert assessment of the organoleptic indicators (Table 2) has found that granulated fillers are the granules of a spherical shape, uniform in size, elastic, without damage. The color of the new product was estimated to be homogeneous, there is pronounced transparency, the absence of gray shades and a diversity of colors. The odor and taste were evaluated to be pure, without foreign odors and aftertaste, with an unexpressed taste.

Table 2

Organoleptic parameters of granulated fillers

Parameter title	Characteristics of granulated fillers
Physical appearance and consistency	The product has a spherical shape in the form of granules, slightly interconnected by the liquid separated from it. The size of individual granules is (2.0...10.0)·10 ⁻³ m. The consistency is elastic, homogeneous throughout the entire volume, granules are easily separated from each other. Surface humidity is allowed, slight separation of moisture
Color	Homogeneous, characteristic of additional raw materials used, gray hues and color diversity are absent
Taste and flavor	Clean, without any foreign flavor and odor, pronounced, characteristic of additional raw materials used

To substantiate the recommendations for the use of granulated fillers in the culinary and confectionery products, we studied their performance in the solutions of sucrose (15 %, 60 %) and organic (citric) acids ($4.5 < \text{pH} < 6.0$). Under these conditions, there is likely to occur a mass exchange between the granules and the liquid, which would affect the properties of the latter. The results of our study of the influence of the technological factors on the module of elasticity and a change in the mass of granules are shown in Fig. 8, 9.

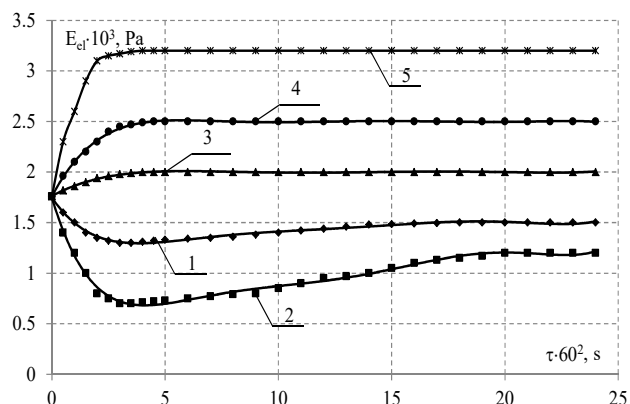


Fig. 8. The dynamics of change in the granulated fillers elasticity module depending on sucrose content (1 – 15 %; 2 – 60 %) and a medium pH (3 – 6.0; 4 – 5.0; 5 – 4.0)

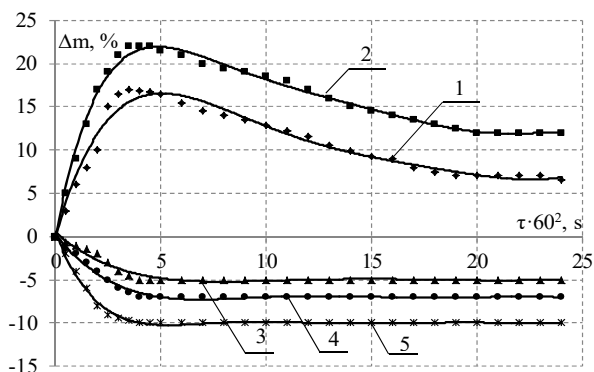


Fig. 9. The dynamics of change in the weight of granulated fillers depending on sucrose content (1 – 15 %; 2 – 60 %) and a medium pH (3 – 6.0; 4 – 5.0; 5 – 4.0)

It was established that during the immersion of granulated fillers into sugar solutions there is a diffusion of molecules of sucrose inside the granules, the consequence of which is branching of the polymer chains of alginate salts. This is confirmed by the results of studying the dynamics of change in the elasticity module and mass of the granulated fillers. The data in Fig. 8 show that over the first $(3...5) \cdot 60^2$ s there is a reduction in the module of elasticity of the granules, regardless of the concentration of sucrose in the solution; the effect increases with an increase in its concentration and the duration of exposure. This stage is characterized as highly dynamic, given the diffusion of sucrose to fillers, there is a rapid reduction in elasticity module by 18 % and 59 % at a content of sucrose in the syrup of 15 % and 60 %, respectively. Subsequently, when the system reaches a concentration equilibrium in terms of sucrose content, there is a monotonous increase in elasticity module. It is likely that under these conditions the low molecular molecules of sucrose that have a spatial structure contribute to the reduction of

hydrogen bonds in the system. Even though the structure formation of fillers is based on the ionotropic gelation, sucrose promotes the “loosening” of the system.

The defined patterns of change in the weight of granulated fillers (Fig. 9) to some extent correlate with the dynamics of change in the elasticity module. Thus, over the first $(3...5) \cdot 60^2$ s, there is a mass gain by the granules by 16...22 % of the initial value, followed by its gradual decrease. The shape of the curves demonstrates that in the first stage there is a diffusion transition of sucrose from syrup to the granules, achieving the state of concentration equilibrium. Next, probably due to the dehydrating influence of sucrose on the system, the mass decreases, but this process is slow and almost stops over $(15...17) \cdot 60^2$ s.

Another regularity of a weight change was established during the aging of the granulated fillers in solutions of citric acid in the pH interval of 4.0...6.0. It was determined that regardless of a pH value there is an increase in the module of elasticity of the granules and, consequently, the reduction of their mass (Fig. 8). The obtained results are explained by the properties of calcium alginate to compact in an acidic environment with a partial release of moisture.

We have investigated the influence of heat treatment ($t=85...87^\circ\text{C}$) on changes in the elasticity and mass of the granulated fillers. It was established that under the general patterns there is an insignificant increase in the module of elasticity (0.7...0.9 %) and a decrease in weight (1.0...1.2 %) to the initial values of indicators.

6. Discussion of results of devising the technological principles for making granulated fillers

By summarizing the results of our study, it is possible to define the basic technological principles for the production of granulated fillers based on sodium alginate:

- the rational use of gel-forming raw materials: the G-block content in the composition of sodium alginate should be within 20...25 %, which is determined by the manufacturer of sodium alginate, or is established experimentally based on the rate of the process of gelation (Fig. 1);

- ensuring a sufficient amount of reacting substances and their concentration nonequilibrium, at which there is a diffusion of calcium ions inside the granules with thus obtaining the granulated products;

- the procedure of adding the reacting components;

- the compatibility of food ingredients in the system, that is, accounting for the influence of food ingredients on the objective course of the reaction of ionotropic gelation.

The undoubted advantage of this study is determining the technological principles for making granulated fillers production as a basic component for the type of a specific technology. However, one of the limiting factors for the proposed technological solutions is the low value of pH for both the receiving environment and the formulation mixture for granule formation (Fig. 1, 3). Under these conditions, the process of granule formation proceeds slowly, which adversely affects the formation of organoleptic and structural and mechanical properties of the resulting product. In addition, a significant limitation in a given technology is the high content of calcium in the composition of raw materials (Table 1). In particular, its presence in the ionic form significantly accelerates the reaction of gelation and makes the prolonged extrusion impossible, during which the structural-mechan-

ical, physical-chemical quality indicators and geometrical sizes of spherical objects are formed.

It is promising from a scientific and practical point of view to implement the devised technological principles for making granulated products not only in food technologies but also in the pharmaceutical and cosmetic industries to produce medicines, vitamins and mineral dietary supplements, enzymes complexes and the complexes of biologically active substances, including those that demonstrate a cosmetic effect.

7. Conclusions

1. It has been determined that the basic condition for obtaining alginate calcium complexes is to implement the sorption processes of calcium ions by sodium alginate. We have defined the factors (the content of guluronic residues in the composition of sodium alginate, the mass proportion of calcium ions, the procedure to introduce reacting components, the duration of exposure in the forming solution), which influence the process of granulation. It has been proven that in order to ensure the progress of sorption processes, the content of G-blocks in the composition of sodium alginate should be 20...25 %, and the content of calcium ions – 10...120 mg %. It has been confirmed that the sorption processes most effectively occur over the first 10-60 s with the gradual slowing and termination of the process, which is regulated by the concentration and sorption capacity of sodium alginate.

2. The generalization of experimental data on the influence of pH on the sorption ability of sodium alginate, the structural and mechanical properties of gels and the effort

of their detachment from the surface of a CaCl₂ solution allowed us to determine the rational parameters for making granulated products based on sodium alginate and calcium ions. It was determined that the rational pH value of the medium is 5.5...7.0, a sodium alginate concentration of 1.0...1.5 %, and ionic calcium concentration of 45...80 mg %, the duration of the granulation process is (2...5)·60 s. Such parameters ensure the most effective sorption of calcium ions with the extraction of granules that have such structural and mechanical properties (a module of elasticity is (5...11)·10³ Pa·s) that are easily detached from the forming environment (a detachment effort is 20.0...32.0 Pa).

3. We have built a model of the technological system and the technological principles for making granulated fillers. It was established that the general regularities in the course of a granulation process can be implemented in a wide range of granulated fillers based both on the raw materials of plant and animal origin and on the highly concentrated saccharin- and alcohol-containing systems at a slight adjustment of the technological process parameters.

4. We have examined the influence of sugar syrups, a medium's pH, and heat treatment, on the module of elasticity and a change in the weight of the granulated fillers. It was established that at a decrease in pH from 6.0 to 4.0 there is an increase in elasticity module from 1.7·10³ Pa·s to 3.3·10³ Pa·s at a simultaneous weight reduction in granules by 10 %. The opposite dependence is observed under the influence of concentrated sugar syrups – a decrease in the elasticity module by 58 % and an increase in the mass of granules by 23 %. During thermal treatment, under the general patterns, there is an insignificant increase in the elasticity module (by 0.7...0.9 %) and a decrease in the mass (1.0...1.2 %) to the initial indicator values.

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