Chapter 9

THEORETICAL AND PRACTICAL ASPECTS OF NATIVE STARCHES USING IN THE TECHNOLOGY OF FOOD PRODUCTS WITH A HETEROGENEOUS STRUCTURE

Hrynchenko O. O.

DOI https://doi.org/10.30525/978-9934-26-445-0-9

INTRODUCTION

In most of the developed countries of the world, there is clearly a tendency to reduce time spent on food preparation to a minimum. This fact became the impetus for the emergence and development of the industry for the production of ready-to-eat products – snacks, salads, soups, desserts, sauces, etc. One of the issues that needs to be resolved under these conditions is ensuring the technological stability of food systems during storage. Being a part of multi-component food systems, which are subjected to various types of processing in the technological flow of production, starch is affected by various technological factors.

It has been analytically prove[1] that the stabilization of the technological properties of food systems, including those based on gelatinized starch dispersions (GSD), is usually achieved through the use of functional technological ingredients (FTI) – thickeners, emulsifiers, stabilizers, the use of which contributes formation of the necessary structure and ensures its stability in the technological flow [2]. However, today's requirements – creation of products with a "clean label", import suabstitution, rational use of national raw resources dictate the need to develop and implement new principles of FTI application. Due to the multi-vector nature of the solution to this task, one of them lies in the plane of creating functional compositions (FC).

Starch in its essence is a unique natural formation that has a biological and physical structure and at the same time consists of two natural polymers – amylose and amylopectin. The uniqueness of starch lies in the fact that the functional properties of its constituent polysaccharides – the ability to dissolve

---

[1] Теоретичні та прикладні аспекти стабілізації харчових продуктів з гетерогенною структурою: монографія / Гринченко О.О., Пивоваров П.П., Михайлов В.М., Погожих М.І. Х: ХДУХТ, 2010. – 254 с.

and swell – cannot be realized as long as its native structure exists. And this means that in order to realize these properties, the native structure of starch must be destroyed, which is ensured by hydrothermal treatment with the formation of a gelatinized starch dispersion. On the way of release of amylose and amylopectin from the structure of starch grains, the latter undergo a series of changes. At the same time, the direction of transformations depends on many factors, but is necessarily accompanied by the absorption of water by starch grains and the development of their surface. Reasonable replacement of water with FTI solution during gelatinization of starch is likely to significantly change the properties of GSD and lead to the formation of a new structure – FC due to sorption of FTI on the surface of starch grains. The intensity and effectiveness of the effect of FTI on the properties of GSD during the formation of FC depends on both the type of FTI and the methods of obtaining the functional composition of starch-FTI. The most pronounced effect of FTI on starch is revealed only under the condition of gelatinization of starch in the FTI solution, resulting in FC with general (by starch component) and individual (by FTI) properties is formed[2].

From the point of view of the FC composition, the functional and other food ingredients used must ensure the course of the necessary processes both within the limits of individual stages – dissolution, emulsification, gelatinization, stabilization, and technology as a whole. It should be clarified that we are talking about a complex of properties that contribute to the intensification and industrialization of processes that ensure technological stability, form the desired texture and organoleptic indicators[3]. Separately, we should focus on the ability of FC to regulate the organoleptic, structural-mechanical and technological properties of the product, to withstand various methods of technological influence in the composition of food products – mixing at the required temperatures, various types of heat treatment (cooking, pasteurization, frying, baking, cooling, freezing) etc. In this case, the thermal stability of food products in a wide range of temperatures under thermal influence in air, water or oil environments must be ensured already at the stage of FC creation[4].

Thus, taking into account modern theoretical and applied aspects of food production and ensuring its technological stability over time, the main technological requirements for FC are as follows:

---

[2] Lee MH, Baek MH, Cha DS, Park HJ, Lim ST. Freeze–thaw stabilization of sweet potato starch gel by polysaccharide gums. Food Hydrocoll. 2002;16:345–52.

[3] Nawab A, Alam F, Haq MA, Hasnain A. Effect of guar na xantham gums on functional properties of mango (Mangifera indica) kernel starch. Int J Biol Macromol. 2016;92:630–5.

[4] Янчева М.О., Желєва Т.С., Погожих М.І., Гринченко О.О. Кріоскопічні дослідження розчинів харчових інгредієнтів полісахаридної природи // Східно-Європейський журнал передових технологій, 2016. – Volume 4. Issue 2. – P. 299– 309.

‒ formation of a complex of necessary organoleptic, physico-chemical and microbiological characteristics in the composition of food products;

‒ intensification of the technological process;

‒ ensuring the suitability of food products for various types of technological processing;

‒ formation of technological and microbiological stability of finished products during storage;

‒ no toxic effect on the human body;

‒ availability of a raw material base, low cost of the raw materials used.

An important aspect during the development of semi-finished products of functional compositions is the use of available, domestic, inexpensive and multifunctional raw materials. The above determines the interest in studying the possibility of using substances of a polysaccharide nature as part of FC, in particular, such as starches, cellulose and its derivatives, gums of plant and microbiological origin, pectin substances, alginates, etc. Raw materials for the production of most of them (starch, cellulose) are not limited; the content in many food products (the exception is starch) is low (0.1...2.0%), most of them (cellulose and its derivatives, pectin substances, alginate) perform important physiological functions.

The use of some FTIs in their native form in the modern food industry is limited due to the impossibility of ensuring the necessary properties of finished products. Modification of the native properties of food systems during directed chemical, physical, biological and/or complex impact is used to expand opportunities, which is widely used in the food and processing industries of the national economy.

Therefore, the replacement of water in the process of gelatinization with a solution of non-starch hydrocolloids (NSH) will allow us to obtain a new type of final product after gelatinization, which in a general sense has properties of GSD, but additionally acquires properties of NSH. A wide range of FTI, the ability to adjust the ratio of components and process parameters on the same principle will allow to obtain a wide range of new products, and its acquisition of new functional and technological properties will allow to develop new technologies of food products on its basis. The development and implementation of the working hypothesis determined the choice and justification of the type of FTI used in the form of non-starch hydrocolloids, as well as the method of obtaining FC based on starch. The choice of FTIs was based, first of all, on the economic and technological aspects of their production and use.[5]

---

[5] Satrapai S, Suphantharika M. Influence of spent brewer’s yeastglucan on gelatinization and retrogradation of rice starch. Carbohyd Polym. 2007;67:500–10.

1. Theoretical model and provisioning mechanism technological stability of starch-based food systems

Gelatinized starch dispersions, which have a significant effect on the textural characteristics of the product, cannot be used in food technology due to the instability of their properties over time, associated with the processes of retrogradation of starch polysaccharides. The creation of FC can be realized by sorption of NSH previously dissolved in water on the phase distribution surfaces arising in the process of gelatinization due to the "molecular sieve" effect. The high sorption capacity of starch during hydrothermal treatment and at the same time the developing surface of starch grains will allow sorption of dissolved NSH, locally increasing their concentration on the surfaces.[6]

In order to establish the mechanism of FC formation, the process of GSD formation from the two-component system "starch-water" was considered, and thermodynamic factors of instability of its properties over time were determined. In the technological flow, the formation of the FC structure based on starch and its change over time can be conventionally divided into three stages:

1st stage – formation of the structure of GSD (gelatinization of starch in water) or FC starch-NSH (gelatinization of starch in a solution of NSH);

2nd stage – reaching a quasi-equilibrium state of the system (a thermodynamic state in which the parameters of the state of the system at the boundary of the phase distribution are such that they correspond to the parameters of the environment) and ensuring it over time;

3rd stage – loss of GSD or FC of the quasi-equilibrium state ("aging" of the system).

According to the theoretical provisions of thermodynamics, the equilibrium state of food products with a heterogeneous structure can be achieved if the condition of equality of chemical potentials of individual components is fulfilled: for GSD – starch and water, for FC – starch, NSH and water.

Conventionally, we denote the starch–water mixture as HMWC–water (according to $T = const$), ignoring the fact that amylose and amylopectin, which differ in properties, are present in the starch structure. At the beginning of the technological process at t = 1...60ºC, starch and water are a mechanical mixture that is practically unrelated in terms of the mass exchange component. According to the provisions of thermodynamics, such a mixture can remain in equilibrium for a long time under given external conditions, and the number of moles of components can be any. Factors of kinship are intense external parameters – P (pressure) and T (temperature). The main adjustable parameter

---

[6] Теоретичні та прикладні аспекти стабілізації харчових продуктів з гетерогенною структурою: монографія / Гринченко О.О., Пивоваров П.П., Михайлов В.М., Погожих М.І. Х: ХДУХТ, 2010. – 254 с.

during gelatinization of starch is temperature. At temperatures above the gelatinization temperature, a change in the state of the HMWC (high molecular weight compounds) occurs, which consists in the swelling and simultaneous activation of hydrophilic areas of macromolecules through their structural release.

Therefore, the essence of the first stage of the technological flow (corresponding in the technological sense to the process of gelatinization of starch) is the desire of starch under the influence of temperature to dissolve. At the same time, the HMWC will tend to decrease the chemical potential, and water will tend to increase, as a result of which there will be a loss of the original packing of the HMWC (HMWC ⇒ $dS > 0$) and the acquisition of order (orderliness) by water ($H_2O \Rightarrow dS < 0$).

It is fair to say that the rate of entropy change (S) for HMWC will be less than that for water $\left|\left(\frac{\partial S}{\partial \tau}\right)_{BMC}\right| < \left|\left(\frac{\partial S}{\partial \tau}\right)_{H_2O}\right|$, since starch polymers are less mobile than water molecules. This is the main principle of creating the general structure of two substances mixture that are in solid and liquid states. If we take into account that the main asymptotics of the probability (w_{Δ}) of thermodynamic evolution is estimated by Einstein's equation $\omega_{\Delta} \approx e^{S_1 - S_0} \approx e^{\Delta S}$, then it should be expected that it is the molecules of water (solvent) at this stage that will determine the formation of the subsequent structure. As a result, water will penetrate inside the starch grains faster than the structural components of the starch grains will diffuse into the water. The consequence of this is the sorption of water by starch from a mixture of starch and water

The directionality of the process of equalizing the concentrations of the components in the volume of the system, that is, the tendency of starch to "liquefy" and water to "solidify", will be preserved throughout this stage. In the initial period, "liquefaction" of starch will occur slowly, which in general will lead to the sorption of water by starch grains. This is very important from the point of view of understanding the sorption mechanism of FC structure formation, because the existing dynamics of the process will allow starch grains to sorb not only water, but also substances dissolved in it, the molar mass of which is less than the molar mass of starch polychains.

The result of gelatinization will be the maximum possible equalization of the chemical potentials of the components ($\mu^{BMC} \Leftrightarrow \mu^{H_2O}$); at the same time, an increase in the concentration of HMWC and a decrease in the concentration of the "free" solvent will lead to the formation of an GSD structure. However, due to the existing structure of the HMWC and the presence in its composition of amylose and amylopectin, which are characterized by different values of chemical potentials, during gelatinization it is not possible to achieve a structure closest to the structure of the solution, which is the reason for its instability over time[7].

Directly, the gelatinization stage takes place at temperatures that exceed the initial starch gelatinization temperature. If we imagine that there is some initial boundary of the starch grain-solvent phase distribution in the GSD (in particular, swollen starch grains), through which the exchange of solvent and solute occurs, then we can apply the so-called coupling equations (for the adiabatic shell), which actually describe the state of equilibrium in the GSD:

$$dS_{BMC} + dS_{H_2O} = 0\,, \tag{1}$$

$$dm_{H_2O}^{(BMC)} + dm_{H_2O}^{(H_2O)} = 0\,. \tag{2}$$

These equations represent the entropy balance of the processes near the equilibrium state and the mass change in the bulk phases of water and HMWC (superscripts in equation 2). Taking into account the theorem of I. Prigozhin on stationary flows, the state described by equations 1, 2 can be reached in case of complete swelling of starch grains and release (activation) of hydrophilic groups. The resulting stationary (diffusive) flow of water ↔ the boundary of the phase distribution reduces or completely eliminates the production of entropy in the system due to a change in the configuration of starch polychains.

When the changes in the free energy of the HMWC and water stop, the stage of the quasi-equilibrium state occurs, designated by us as the second stage, during which any processes inside the system do not change the free energy, except for the energy of the surface layers, the properties of which are determined by the surface tension at the boundaries of the phase distribution. From this it follows that the stability of GSD or FC starch-NSH will depend on the area of phase distribution and the amount of energy of the surface layers that is not compensated by the external phase. The inhomogeneity of dimensional characteristics of starch grains in native starch, the presence of structural anomalies in the form of various inhomogeneities of grain packing are the reason for the formation of GSD with a heterogeneous structure by volume, characterized by the presence of a huge area of phase distribution. In addition, not only starch grains, but also component polysaccharides, which are characterized by different properties and colloidal state, will participate in the creation of the phase distribution surface. Under the condition of various solubility, the low-molecular fraction of starch – amylose, as it is less

---

[7] Теоретичні та прикладні аспекти стабілізації харчових продуктів з гетерогенною структурою: монографія / Гринченко О.О., Пивоваров П.П., Михайлов В.М., Погожих М.І. Х: ХДУХТ, 2010. – 254 с.

hydrophilic, forms a solution (sol), which will be separated from the solvent by the micelle-like structure of amylopectin.

The factor of instability and loss of the quasi-equilibrium state can be an uneven distribution of uncompensated free energy, while the existing phase separation surface will be characterized by an individual amount of free energy. This will be especially evident in the case of using starch with polydisperse characteristics. A different rate of change of free energy will lead to the formation of local maxima of free energy or to the so-called "bifurcation points". Bifurcation can lead to coagulation of HMWC and their displacement from the solution, that is, to the destruction of the structure of the GSD. This process is the result of the loss of affinity between the HMWC and the solvent.

The duration of the existence of GSD in a quasi-equilibrium state will be determined by the affinity of HMWC–water on the phase distribution, or more precisely, by the relationship of HMWC to the solvent. This value can be characterized by the value of the surface tension arising from the lack of compensation from the outside. In the case of an increase in the affinity of the HMWC and the solvent on the surface of the phase distribution, which means a decrease in the free energy and surface tension, the stability of the dispersed system will increase. It follows from this that the replacement at the boundary of the distribution of the phases of the HMWC (starch, amylose, amylopectin), capable of deteriorating their affinity with water over time, with other, more hydrophilic, stable over time HMWC, such as highly hydrophilic NSH, will allow not only to reach a quasi-equilibrium state, but also to ensure its existence in the technological flow. Substitution of surface layers at the boundary of the phase distribution with more hydrophilic NSH can be carried out only by sorption. This well-known fact in physical chemistry can be used to ensure the technological stability of food products based on starch. The stability of GSD or FC starch–NSH and the duration of their existence in the metastable state will be determined by the conditions of stationary equilibrium:

$$\frac{dF}{d\tau} = 0, \quad \frac{dS}{d\tau} = 0, \tag{3}$$

but for F it is a striving for the minimum, and for S – for the maximum. That is, the variations of free energy and entropy near this point are as follows:

$$(\delta F)_E > 0, \quad (\delta S)_E < 0, \tag{4}$$

where E – total energy in the system.

The kinetics of this process can be represented in the form of a dynamic balance of diffusive water flows "to" and "from" the HMWC. In a quasi-equilibrium state, the sum of the flow vectors is zero. The inequality of these flows will lead to "aging" of the system. Determining the nature of these flows (j_S) is rather difficult, because the cause of their occurrence can be many factors – from mechanical (deformation of the structure, dispersion) to electromagnetic and quantum (change in interaction potentials, irradiation, etc.). The simplest can be an assumption about fluctuations due to the Brownian motion of an element of the structure of a micelle-like formation. The stated provisions are valid for the structure of GSD, as well as FC starch–NSH and can be proved by theoretical and experimental studies

2. Theoretical and experimental confirmation of the mechanism of FC formation based on starch

One of the proofs of the FC formation mechanism is based on consideration of the properties of starch in relation to its dispersion and grain packing structure, which determine both the size of the emerging distribution surfaces and the size of local energy maxima. Topographic heterogeneity can be imagined in the form of starch grains with dense and loose packing. A hypothetically densely packed grain can be imagined as a sphere with a pronounced outer surface; starch with loose packaging – in the form of a sphere with simultaneously present external and internal surfaces (Fig. 1, a, b). The inner surface of loosely packed starch grains can be formed both at the stage of photosynthesis and in the technological flow. It can be of any shape, but for calculations it is advisable to imagine it in the form of a hollow sphere (Fig. 1, b).

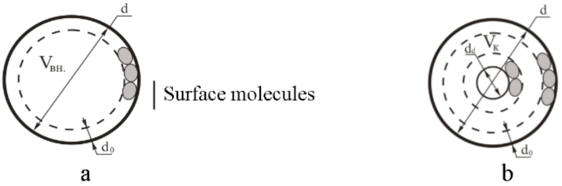


Fig. 1. Model of a starch grain densely packed (a) and with an internal cavity – loosely packed (b)

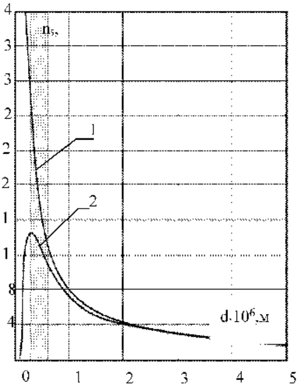


Fig. 2. Relative number of surface molecules depending on the diameter of starch grains: 1 – for dense grains; 2 – for grains with loose packaging

Proceeding from the equilibrium state inside the grain, ignoring the heterogeneity of the component composition of starch, which corresponds to the minimum of free energy, fundamentally, it is possible to determine the surface area of the phase distribution of "starch-water" systems in GSD. Regardless of the assumption about the geometric shape of starch grains, it is important to determine the so-called "surface" molecules, which, in contact with the external environment, form a surface potential or free energy, the local minimum of which determines the achievement and duration of the existence of GSD in a quasi-equilibrium state. The specific value of the surface potential will be greater, the greater the ratio of the total number of "surface" molecules to their total number. If this value, which characterizes the relative number of "surface" (n_S^*) molecules to their total number (n), is denoted as n_S, then it can be calculated for starch grains with different packing of molecules according to the formula

$$n_S{*} = 1 - \frac{\left(\sqrt[3]{n} - 2\right)^3}{n}. \qquad (5)$$

According to the conducted theoretical studies, it can be stated that both the dispersion of starch and the structure and density of grain packing determine its behavior in the technological flow. It can be seen from the data in Fig. 2 that the role of surface molecules increases during the increase in grain dispersion and sharply decreases during the growth of the "internal cavity" for small grains. From the point of view of the occurrence of local extremes of the free surface energy, it becomes obvious that the duration of the existence of GSD in a quasi-equilibrium state under the condition of using starch grains with different dispersions will be insignificant due to the probability of the occurrence of bifurcations.

The above determines the expediency of using starch with a narrow particle size distribution in the technological flow, and from the point of view of ensuring the stability of the systems, the starch grains must be clearly dispersed. These facts clearly justify the choice of starch – potato, corn, rice, etc. taking into account their dispersity and homogeneity for native polymodality. The proof of the relationship between the dispersion of starch grains and the stability of starch-based systems is experimental data from the study of the influence of the dispersion of starch grains on the GSD viscosity (Fig. 3).

The thixotropy of OKD on amylograph curves is manifested in the values of maximum (η_{ma}) and minimum (η_{min}) viscosity. The decrease in viscosity (aspiration $\eta_{ma} \Rightarrow \eta_{min}$) at a given speed gradient continues until the structural lattice takes the form of a stationary state, and the difference η_{ma} and η_{min} indicates the degree of destruction of structural elements under the influence of mechanical stresses and thermolysis. The approach of η_{min} to η_{ma} indicates the stability of the structure created in the process of gelatization.

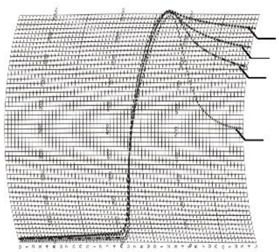


Fig. 3. Amylogram of changes in the viscosity of GSD based on starch with grain diameter, м: 1 – $(1…3)\times10^{-6}$; 2 – $(4…6)\times10^{-6}$; 3 – $(7…14)\times10^{-6}$; 4 – control

It was established that the decrease in the diameter of starch grains is accompanied by a decrease in the temperature gelatization of starch dispersions. Obviously, this fact is due to the entropy factor: the degree of order of molecules on the surface of highly dispersed particles is higher than that of low-dispersed ones, where the heterogeneity of chemical bonds leads to greater chaos in the energy levels: the depth of the potential "pit" decreases, and the "pit" itself expands (in relation to the effective radius of interaction with the solvent). In the latter case, gelatization of starch begins at a lower temperature with the effect of swelling of starch grains, which is more significant than for highly dispersed systems. It can be expected that for d < 1 $\cdot 10^{-6}$ m, the thixotropic effect for GSD will disappear, and the stability of the structure will increase even at lower concentrations of starch. On the contrary, if the diameter of starch grains increases, their instability will be more pronounced.

The proof of the mechanism of the structure formation of the FC starch–NSH, as mentioned earlier, is based on the consideration of the gelatization process of starch as an adsorption process at the boundary of the liquid–solid phase distribution (in our case, represented by water or a solution of NSH and a starch grain).

The considered model two-component system can also be applied in the case of a three– or multi-component system. For this, the solvent (water) can be replaced by another solvent, for example, a solution of NSH. The molar mass of NSH should be less than the molar mass of the dissolved substance (starch). If we assume that thermal equilibrium is achieved during the sorption process, $de^{S'} = 0$, dT = or $d\sigma = -\sum_i \Gamma_i \cdot d\mu_i$. This is the well-known Gibbs equation, which for a two-component mixture has the form:

$$d\sigma = -\Gamma_1 \cdot d\mu_1 - \Gamma_2 \cdot d\mu_2 . \tag{6}$$

Враховуючи, що для ізотермічних умов $d\mu = RT \cdot d(\ln C)$, та провівши область поверхні розподілу там, де надлишок першого компонента вирівнюється з відповідною об'ємної фазою, отримаємо $\Gamma_1 = 0$. Тоді

$$d\sigma = -\Gamma_2 \cdot d\mu_2 = -\Gamma_2 \cdot RT \frac{dC}{C}, \tag{7}$$

тобто

$\Gamma_2 = -\frac{C}{RT} \cdot \frac{d\sigma}{dC}$, Given that for isothermal conditions $d\mu = RT \cdot d(\ln C)$, and drawing the region of the distribution surface where the excess of the first component is aligned with the corresponding bulk phase, we obtain $\Gamma_1 = 0$. Then

$$d\sigma = -\Gamma_2 \cdot d\mu_2 = -\Gamma_2 \cdot RT \frac{dC}{C}, \tag{7}$$

that is

$$\Gamma_2 = -\frac{C}{RT} \cdot \frac{d\sigma}{dC}, \tag{8}$$

where C – concentration (equilibrium) of the dissolved substance.

Two main conclusions emerge from equation 6:

1. Adsorption depends on the temperature ($\Gamma = f\ (\frac{1}{T})$. For the three-component system starch–water–NSH, the process of gelatization of starch

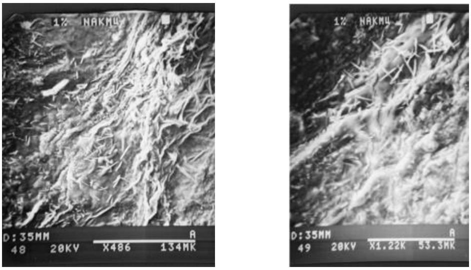
dispersions at different temperatures (or holding at fixed temperatures) will objectively be accompanied by a different degree of sorption. Therefore, as the temperature of obtaining FC starch–NSH, as well as the time of holding the mixture at a given temperature will determine the different degree of modification of GSD and are important parameters during the creation of a FC with given properties. An increase in temperature is a necessary condition for the formation of FC, which confirms the impossibility of obtaining semi-finished products only by mixing components

2. Since $\frac{d\sigma}{dC}$ can have both negative and positive values, Γ_2 can also have both negative and positive values. When $\Gamma_2 > 0$, the concentration of pre-dissolved NSH in the surface layers of the starch dispersion will increase compared to the bulk phase, which confirms the hypothesis put forward regarding the increase in the concentration of NSH on the developing starch surfaces. When $\Gamma_2 < 0$, the concentration of NSH decreases

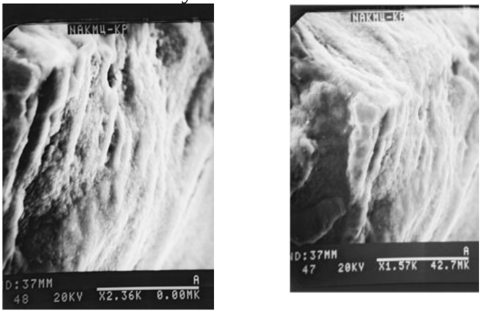
By adjusting the characteristics of the solid substance (starch) (size, packing density, etc.), selecting the solvent by changing the components of the solution, adjusting the parameters (temperature, increasing the affinity between the components, the sequence of introducing the components, etc.), it is possible to form more hydrophilic substances on the surface of the starch–solvent distribution due to sorption processes and thereby regulate the ability to self-disperse or sediment in a heterogeneous system.The established regularities will make it possible to select the conditions of sorption (dissolution, swelling, sedimentation) in starch–water or starch–NSH systems under the condition of $\Gamma_2 > 0$ (dissolution, swelling) or desorption under the condition of $\Gamma_2 < 0$ (sedimentation), as well as to increase (regulate) dissolution rate of NSH.

In the case of the creation of FC starch-NSH, the concept of "selection of solvent" is reduced to the selection of the type of NSHand the establishment of its rational concentration. In the group of NSH, there are polysaccharides that can affect the surface tension of aqueous solutions to varying degrees, which means that they have different sorption capacities.

The theoretically predicted sorption mechanism for the formation of FC starch–NSH was confirmed experimentally. In fig. 4 shows the results of electron microscopy of dehydrated NaCMC (Na-carboxymethylcellulose) films and FC starch–NaCMC obtained by gelatization of 10% starch suspensions in a 1.0% NaCMC solution. From the analysis of the data, it can be seen that an important condition for the creation of FC is the state of NaCMC (Fig. 5.4, a). It can be seen that it is not always possible to completely dissolve NaCMC even at a concentration of 1.0%. Therefore, in dehydrated NaCMC films, undissolved NaCMC aggregates with a needle-like structure are detected, which are well registered both in the case of an increase of 486 and 1220 times.



a – dehydrated NaCMC films



b – dehydrated FC starch–NaCMC

Fig. 4. Fragments of the microstructure of dehydrated NaCMC films (a – magnification 486 and 1220 times) and FC starch–NaCMC (b – magnification 1890 and 2360 times)

Under the conditions of magnification of 1890 and 2360 times, it can be seen that the surface of FC is quite homogeneous, it is characterized by a folded structure without visible cracks, depressions, and shells. When the sample is shaken inside the FC, radial pores located perpendicular to the surface are revealed. Pores are registered both at a magnification of 1,570 times, and more clearly at a magnification of 2,360 times. It can be seen that inside the starch grain is more heterogeneous than the surface, which can be attributed to sorption on the surface of NaCMC. And these are not artifacts from dehydration. Presumably, there was structurally free water inside the system, which was a structural element of the GSD.

Since the dehydration of the samples did not change their geometric dimensions, pores were formed in the places of water localization. Due to the sorption effect of NaCMC and the presence of the "molecular sieve" effect, this water cannot be a solvent and a medium for NSH diffusion, therefore, after drying, only a dry matrix is preserved, which, as a "negative", prints the structure of water in FC. The difference in the topography of the samples is a confirmation of the sorption mechanism of FC formation. It is important that the concentration of NaCMC on the surface of starch grains does not cause salting out and does not crystallize NaCMC. It can be seen that the system is homogeneous in composition, i.e. joint gelatinization increases the affinity and the system acquires a "reticulated" structure instead of forming a mixture. It is impossible to achieve such uniformity by mixing.

Convincing proof of the mechanism of formation of FC starch–NSH by sorption is the study of the molecular masses of the complex components of starch – amylose and amylopectin, systems obtained by mixing GSD and solutions of NSH, as well as FC starch–NSH.

In the pre-prepared NSH solution (at the 1st stage), under conditions of solvent excess, there is an equilibrium between the solvation of NSH molecules and their mutual association, which determines the structural and mechanical properties of the solution, its resistance to sedimentation and, ultimately, the duration of the existence of the solution in quasi-equilibrium condition.

In the process of mixing two solutions of HMWC (gelatization of starch in the NSH solution at the 2nd stage), the equilibrium that exists in each of the solutions between the solvent and HMWC, as well as between the solvation of HMWC molecules and their mutual association, is shifted towards HMWC, which have a greater hydrophilicity. This process is accompanied by the emergence of hydrophobic interactions. In our opinion, hydrophobicity in this case should be considered as the ability of one of the HMWC (starch at gelatization temperatures) to bind an excessive amount of solvent, displacing from the same solvent the HMWC that have a lower affinity with it under these conditions, which can lead to a certain type of association of polymer molecules and an increase in the molecular weight of associates compared to the original ones. Such an interaction in the presence of a solvent, as a rule, cannot lead to the salting out of one of the HMWC from the solution, while in the case of concentration of the HMWC, an association with a pronounced colloidal effect of precipitation is possible.

The consequence of the binding effect of water is a decrease in the Brownian motion of the HMWC in the solvent, which leads to the emergence of a stabilization effect and an increase in the duration of the system's existence in a quasi-equilibrium state. The validity of our reasoning is confirmed by the study of the molecular mass characteristics of NSH (using the example of NaCMC), amylose and amylopectin (as the main starch polysaccharides), as well as the systems amylose–NaCMC, amylopectin–NaCMC (Table 1).

Table 1

Molecular mass distribution of amylose, amylopectin and GSD

Fractions,m.w. *	**Content of fractions, %**		
	amylose	**amylopectin**	**GSD**
15000	6,3	4,5	8,7
20000	10,1	28,8	40,4
40000	19,4	28,9	1,5
70000	26,8	11,5	9,0
110000	21,3	3,7	5,1
500000	15,7	7,1	14,7
100000	0,4	4,8	4,5
2000000	–	10,7	16,1
Total	100,0	100,0	100,0
Average molecular weight, Mw	135415,0	327615,0	462395,0
Note. * Molecular weights of markers			

The analysis of the fractional composition of the systems shows that with an average molecular weight (Mw) of amylose of 135415.0, its composition is dominated by fractions from 20,000 to 500,000, and in the composition of amylopectin (if Mw = 327615.0) – fractions with a molecular weight from 20,000 to 70,000.

The stated assumption about the possible interaction of HMWC with the solvent with the occurrence of hydrophobic interactions is also confirmed during the preparation of FC starch–NSH. If the temperature of the starch–NaCMC suspension rises to a temperature higher than the gelatinization temperature, starch grains are "unpacked" with intense absorption of the solvent. At higher molar concentrations of starch (compared to NSH), due to its tendency at gelatinization temperatures to acquire a state of equilibrium in the solvent, intensive hydration of its constituent polysaccharides and absorption of the solvent from the solution of the HMWC occurs. At the same time, on the one hand, the equilibrium in the solvation of NSH (NaCMC) is disturbed, shifting from NSH–water interaction at the initial stage towards NSH polymer–NSH polymer interactions. The displacement of the solvent from the NSH solution, used for the dissolution and hydration of starch polysaccharides, leads to the displacement of NSH molecules from the solution, the emergence of hydrophobic interactions between individual macromolecules of NSH. Hydrophobic interactions in this case should be considered as forces of repulsion (displacement) of NSH polymers by water. The consequence of this may be the development of hydrophobic interactions of NSH polymers with the appearance of associates with a higher molecular weight.

On the other hand, intensive development of the surface of starch grains, increasing the concentration of NSH due to the use of a solvent for hydration of starch polymers, lead to the emergence of sorption effects, the consequence of which is the appearance of a layer of partially dehydrated NSH on the surface of starch grains and the development of the interaction between starch-NSH. At the same time, the concentration of NSH in the formed layer is significantly higher than the concentration of NSH in the original solution. In this case, sorption processes become dominant, which leads to the formation of a FC structure and a new colloidal state that differs from an equivalently concentrated mixture of two solutions.

3. Practical implementation of the theoretical model of ensuring the technological stability of starch-based food systems

The conducted theoretical and experimental studies confirm the possibility of creating FC based on starch and are a prerequisite for the development of their recipe composition, basic technological scheme and technological schemes of FC production for "target" technologies[8].

The types and concentration of individual components in the composition of FC are determined by specific technological tasks – the need to carry out processes of emulsification, stabilization, gelatinization, etc. in the composition of food dispersion systems. At the same time, a mandatory condition is the formation of the necessary textural characteristics of the finished food product and ensuring its technological stability over time. The following characteristics are meant by the formation of the necessary textural characteristics of food dispersion systems, including food products:

- for food dispersion systems with an emulsion structure – the content of the fat and water phases, their ratio; the composition of the dispersion medium and the dispersed phase, taking into account a specific technological task, the composition of the dispersion medium from the point of view of texture formation (the presence of fillers, their dispersion) and other organoleptic characteristics – stickiness, fragility, velvety, feeling of wateriness, saturation of taste, speed of flavor release, etc..;
- for food dispersion systems with a gel-like structure – the presence of an elastic, springy or other texture, isotropy or anisotropy of the jelly according to the vector of destruction (crushing) or during visual assessment; the presence of a uniform or different texture by volume (gloss on the surface, gel heterogeneity); the ability to stick together, stretch, resist or undergo deformation forces; presence of heterogeneity in terms of fillers; ability to melt or resistance to melting under the influence of different temperatures, etc.

---

[8] Теоретичні та прикладні аспекти стабілізації харчових продуктів з гетерогенною структурою: монографія / Гринченко О.О., Пивоваров П.П., Михайлов В.М., Погожих М.І. Х: ХДУХТ, 2010. – 254 с.

From the point of view of the formation of functional and technological properties of FC, the concentrations of both starch and NSH can be different, but they are selected in such a way as to ensure positive sorption of NSH on the surface of starch grains during the gelatinization process. Thus, in order to ensure the emulsification of the fat phase, FC semi-finished products should probably have the ability to regulate the surface activity of the recipe mixture, to form low-viscosity systems. Use of FC to stabilize emulsions, foams, suspensions, etc. puts forward the following requirements for them: increasing the structural viscosity of adsorption interphase layers (for emulsions, foams); formation of systems with adjustable viscosity (for suspensions, emulsions, foams); the ability to thixotropically restore the structure after mechanical impact.

The model of the technological system for the production of FC starch-NSH consists of several subsystems and determines the need for their synthesis and research into the functioning of subsystems at the micro level in the following sequence: (C_1, C_2) → B → A. It should be noted that both the type of NSH and the technological parameters of dissolving NSH are individual. When choosing NSH , taking into account the properties of the final food product, we gave preference to such polysaccharides as NaCMC, guar and xanthan gums, pectin, sodium alginate, methylcellulose, dextrins. The solution of NaCMC, guar gum and xanthan gum, pectin, sodium alginate, dextrins is carried out as follows: NSH is combined with water (t = 4...6 ºC), if the hydromodule is 1:(10...15), left to swell and formation of a highly viscous system during (1...2)×3600 s with subsequent heating of the system to t = 98...100 ºC; then the system is cooled to t = 4...6ºC and kept for (20...24)×3600 s until complete dissolution of NSH.

Subsystem C_2 "Formation of starch-NSH dispersion" involves mechanical mixing of the NSH solution and corn starch at temperatures lower than the starch gelatinization temperature (t = 1...60 ºC). It should be emphasized the constantly existing phase incompatibility in the given temperature range of the three-component starch–water–NSH system, which is a sedimentationally unstable suspension. Such a suspension at temperatures below the gelatinization temperature of starch can remain in neutral equilibrium for any length of time

Subsystem B "Formation of the FC starch-NSH system" involves heat treatment of the starch-NSH dispersion at a temperature of 89...91ºC and under the condition of constant stirring, which prevents the sedimentation of starch grains. At the same time, the system will observe the equalization of the chemical potentials of the components, the loss of the original packing of starch grains and the development of surfaces, the activation of the hydrophilic centers of their constituent polysaccharides, the sorption of NSH from the solution on the surface with the formation of a structure characteristic of FC starch–NSH. The existing dynamics of the process allows, in the process of gelatinization due to the sorption of water by starch grains, to first displace NSH due to the "molecular sieve" effect on the surface of the phase distribution of the NSH starch grain solution, and then to sorb them on the developing surfaces. In essence, water becomes a “bad” solvent for NSH, as a result of which a weakly concentrated solution of NSH is transformed on the phase distribution surfaces into a solution of higher concentration, and the three-component system starch–water–NSH itself is transformed into a new state – FC, which is, on in our opinion, a dispersion of swollen starch grains with solubilized NSH adsorbed on their surface.

It is at this stage that the system is in a quasi-equilibrium state, the duration of which, due to the formation of more hydrophilic surfaces and an increase in the affinity between HMWC and water, is much longer than that for GSD. At the same time, it has been experimentally confirmed that starch grains, gelatinized in NSH solution, are characterized by higher dispersion, which increases their stability during storage.

Within the framework of subsystem A "Formation of FC starch-NSH" under the conditions of a general principled approach, the task of creating FC for target technological processes should be solved.

The use of starch and NSH in FC technology determined the need to study their main physico-chemical (including structural-mechanical) and functional-technological characteristics, among which the main ones are viscosity, water-retaining and gel-forming abilities, stability during storage and others.

It has been experimentally proven that the structure formation of GSD during cooling and storage is associated with the formation of a three-dimensional network of hydrogen bonds, the donors and acceptors of which are amylose and amylopectin. The number of hydrogen bonds formed in this case depends on the weight concentration of their donors, which is clearly expressed under the condition of increasing the concentration of starch in GSD. It has been experimentally proven that NSH solutions are liquid-like systems, the viscosity of which at a constant shear rate depends on the concentration, which have, compared to GSD, more stable structural and mechanical properties, depending on the magnitude and nature of the external influence.

A comparison of the established dependences of viscosity on the shear rate in the forward and reverse modes indicates significant differences in the properties of highly concentrated GSD and FC starch–NSH. Due to involuntary structuring and the desire of GSD to acquire solid-like properties, incomplete structural relaxation occurs and the presence of significant irreversible structural effects. The degree of reversibility of the GSD properties after the destruction of the structure depends, first of all, on the concentration of starch, as well as other factors, among which, in our opinion, the temperature of GSD, as well as the duration and conditions of exposure of GSD in the gelatinized state are dominant.

The study of the rheological characteristics of starch dispersions, GSD and FC starch–NSH was carried out on a Brabender amylograph, determining the initial temperature of the dispersion gelatinization, the maximum viscosity and its corresponding temperature, as well as the minimum viscosity, which was recorded after 10 60 s of thermostating the system at t = 95 C.

Table 5.2

Coefficient of thixotropic recovery of the structure of FC starch (10%)–NSH (0.5%)

FC name	**Coefficient of thixotropic recovery of the structure, %**
Starch-NaCMC	65,2±0,3
Starch-MC	63,8±0,2
Starch-guar gum	78,0±0,3
Starch-xanthan gum	83,8±0,4
Starch-sodium alginate	78,2±0,3
Starch-pectin	80,1±0,3

It was experimentally established that FC starch–NSH compared to GSD are characterized by a lower initial temperature of gelatinization, the value of which is determined by both the type of NSH and its concentration. It was established that for all studied systems, depending on the type of NSH, an increase in their concentration in the range of 0.1...0.5% contributes to a decrease in the value of the initial temperature of gelatinization by 1.0...7.5ºC. The most pronounced effect of reducing the initial temperature of gelatinization is characterized by MC ($t_{initial}$ FC starch (10%)–MC (0.5%) is 64.0ºC versus 71.5ºC for GSD), xanthan gum ($t_{initial}$ = 64, 2ºC) and pectin ($t_{initial}$ = 64.9ºC)

The study of the deformation characteristics of FC starch–NSH on Kargin–Sogolova balances confirmed that with an increase in the specific weight of NSH, the overall deformation of the systems increases. It was established that with an increase in the concentration of NSH, the amount of highly elastic deformation increases, that is, the modulus of high elasticity decreases. At the same time, the share of highly elastic deformation in the total deformation decreases, which indicates an increase in plasticity as the content of NSH increases.

It was established that the specific weight of the residual plastic deformation increases with the increase in the content of NSH; at the same time, the cohesive interaction in the systems decreases, because the value of the instantaneous modulus of springiness in the relaxation mode for a partially destroyed system is smaller than the similar indicator in the load mode. This indicator increases as the concentration of NSH in the FC composition increases.

One of the indicators characterizing the formation of a new structure of FC starch–NSH is the technological stability of GSD properties over time. According to theoretical studies, the degree of orderliness of surface molecules of starch grains determines the degree of orderliness in energy levels. In connection with the adsorption processes that take place during the creation of FC, the surface layers of GSD are saturated with adsorbed NSH molecules, which leads to the "replacement" of the composition of the surface layer, consisting of multimolecular amylose and amylopectin in GSD, with a monodisperse layer of NSH in composition. Understanding that a three-dimensional network with the formation of a gel structure is created during the cooling of GSD due to the interactions of surface molecules of amylose and amylopectin, it can be concluded that this ability will be significantly adjusted in FC starch–NSH, which determines a lower level of viscosity "failure" during cooling, which means more stable properties during storage.

Ensuring the technological stability of food products based on FC starch-NSH depends significantly on the affinity of NSH and water. GSD are a complex colloidal system, the properties of which are determined simultaneously by the physical characteristics of starch grains and the properties of amylose and amylopectin. In the process of gelatinization, amylose diffuses into the aqueous phase and tends to equalize the concentration of the substance throughout the volume. Amylopectin, as a substance more hydrophilic than amylose, is able to bind a larger amount of water and thereby hinder the diffusion of amylose. Such a contradiction leads to the fact that in the event of a shortage of water in the system, there is a competition for water. At the same time, amylopectin, binding water, deforms the structure of spiral-like chains of amylose, thereby contributing to the emergence of a tense state within the system.

The degree of tension increases with a decrease in temperature as a result of the occurrence of additional hydrogen bonds, as evidenced by the measurement of the structural and mechanical properties of the systems during cooling. A temporary quasi-equilibrium state arises, which can be disturbed by any external factor. The tendency of amylose to diffuse in the solvent, and amylopectin to bind the solvent, leads to the fact that under certain conditions water becomes a "bad" solvent, displacing amylose into a separate phase capable of spontaneous polymerization due to the formation of hydrogen bonds.

A critically high disequilibrium has the OKD on the starch grain–water phase distribution. On the one hand, the outer layer of the grain, being more densely packed, is less hydrated compared to the inner layers, on the other hand, it is not compensated by water for the tensions that arise (free energy, surface forces). The relative excess of water in the outer layer leads to a more complete hydration of the surrounding amylopectin, the consequence of which is a decrease in its interaction with amylose, a decrease in tension with the resulting possibility of diffusion of amylose into the solvent. Such a process, being irreversible, reduces the concentration of amylose near the surface of the starch grain and, presumably, will occur until the amylose concentration equalizes in the volume of the system. However, since the concentration of amylose inside the grain, on the surface of the grain, and in the water (outside the grain) is unlikely to equalize, the diffusion process will take place indefinitely, but at different speeds. It is significant that the metastable state inside the grain will be disturbed, which corresponds to the established amylose-amylopectin balance, as a result of which the system will change irreversibly. Such a process is inevitable at any concentration of starch in GSD. Since water is the most mobile in the three-component system amylose–amylopectin–water, the result of the disturbance of the equilibrium will be a change in the mobility of water.

Studying the mobility and bond forms of water using spin-spin and spin-lattice relaxation confirmed our theoretical and experimental calculations that the adsorption of NSH during the preparation of FC starch–NSH hydrophilizes the surface of starch grains, significantly increasing the affinity for water, and for this reason complicates the diffusion of amylose. The consequence of the formation of a micellar structure of FC with hydrophilized surfaces of starch grains is the formation of a significant area of distribution of phases with a solvent with reduced water mobility, which leads to an increase in the proportion of bound (structured) water, reducing its mobility, as well as the partial pressure of vapors. Conclusions were made about the change in the forms of moisture connection by studying the process of water evaporation from GSD 10% concentration and FC starch (10%)–NSH (0.1...0.5%).

In order to justify the technological use of FC as part of food products, their stability over time at t = 0...6°C, as well as after being exposed to negative temperatures in the "freezing-defrosting" mode, was investigated [4]. Stability was assessed by determining the amount of aqueous phase that was released. The study of the properties of GSD and FC of starch-NSH for 30 days, stored at a temperature of 0...6°C, showed that during storage, the general trend for all samples is a distinct inhibitory effect to the aqueous phase, which was released during storage in all studied FC. The amount of aqueous phase that was released is 1.7...9.3 times smaller for FC compared to GSD equiconcentrated in terms of starch content. The most pronounced stabilizing effect is characterized by xanthan gum and pectin. If their content in FC semi-finished products is 0.3% and 0.5%, no release of the aqueous phase is observed up to 16 days of storage. An increase in the aqueous phase, which is released between the 16th and 30th day of storage, was noted.

The stabilizing effect of NSH as part of FC is also revealed under the conditions of using cyclic freezing-defrosting. It has been proven that in the case of repeated freezing–defrosting of the studied samples, the proportion of the separated aqueous phase increases in all cases. At the same time, the specific weight of one phase, which was separated from FC starch–NSH, is 2.4...2.8 times smaller compared to GSD.

CONCLUSIONS

Thus, the conducted set of studies confirmed the hypothesis we formed about the technological stability of FC starch-NSH. The research results are a convincing experimental prerequisite for ensuring the technological stability of food products using FC based on polysaccharides. A theoretical model and mechanism for ensuring the technological stability of food systems based on native starch has been developed. The mechanism of functional compositions formation based on starch has been theoretically and experimentally confirmed. Recommendations on the practical implementation of the use of native corn starch in the technology of food products have been formulated.

SUMMARY

The ways of using native starches (on the example of corn starch) in the technology of food products have been expanded. It is analytically proven that the stabilization of the technological properties of gelatinized starch dispersions is usually achieved by using functional and technological ingredients. Their use contributes to the formation of the necessary structure and ensures its stability in the technological flow. A theoretical model and mechanism for ensuring the technological stability of food systems based on native starch has been developed. The mechanism of functional compositions formation based on starch has been theoretically and experimentally confirmed. Recommendations on the practical implementation of the use of native corn starch in the technology of food products have been formulated.

Bibliography

1. Теоретичні та прикладні аспекти стабілізації харчових продуктів з гетерогенною структурою: монографія / Гринченко О.О., Пивоваров П.П., Михайлов В.М., Погожих М.І. Х: ХДУХТ, 2010. – 254 с.

2. Lee MH, Baek MH, Cha DS, Park HJ, Lim ST. Freeze–thaw stabilization of sweet potato starch gel by polysaccharide gums. Food Hydrocoll. 2002;16:345–52.

3. Nawab A, Alam F, Haq MA, Hasnain A. Effect of guar na xantham gums on functional properties of mango (Mangifera indica) kernel starch. Int J Biol Macromol. 2016;92:630–5.

4. Янчева М.О., Желєва Т.С., Погожих М.І., Гринченко О.О. Кріоскопічні дослідження розчинів харчових інгредієнтів полісахаридної природи // Східно-Європейський журнал передових технологій, 2016. – Volume 4. Issue 2. – P. 299– 309.

5. Satrapai S, Suphantharika M. Influence of spent brewer’s yeast bglucan on gelatinization and retrogradation of rice starch. Carbohyd Polym. 2007;67:500–10.

6. Pongsawatmanit R, Chantaro P, Nishinari K. Thermal and rheological properties of tapioca starch gels with and without xanthan gum under cold storage. J Food Eng. 2013;117:333–41.

7. Харчові добавки: навчальний посібник. /За заг. ред. Гринченко О.О. /Н. Г. Гринченко, О. П. Неклеса, А. Б. Горальчук, Т. В. Черемська, О. Ю. Рябець, Р. В. Плотнікова, Б. Б. Ботштейн, М. О. Янчева, Р. П. Никифоров Харків: ХДУХТ, 2017. – 420 с.

8. Інноваційні технології виробництва харчової продукції масового споживання: монографія / Пивоваров П.П., Гринченко О.О., Михайлов В.М. та інш. Х.: ХДУХТ, 2011. – 444 с.

9. Physiochemical, Pasting, and Thermal Properties of Starch Isolated from Different Barley Cultivars, International Journal of Food Properties, 16:7, 1494-1506, https://doi.org/10.1080/10942912.2011.595863

10. Camila Delinski Bet, Cristina Soltovski de Oliveira, Cleoci Beninca, Tiago Andre´ Denck Colman, Luiz Gustavo Lacerda, Egon Schnitzle. Influence of the addition of hydrocolloids on the thermal, pasting and structural properties of starch from common vetch seeds (Vicia sativa sp)/ Journal of Thermal Analysis and Calorimetry 32(3): 579-587, jul.-set. 2012

11. Kim HS, Patel B, BeMiller JN. Effects of the amylose-amylopectin ratio on starch hydrocolloids interactions. Carbohyd Polym. 2013;98:1438–48. 43.

12. Byars JA, Singh M, Kenar JA. Effect of hydrocolloids on functional properties of navy bean starch: Effect of hydrocolloids on functional properties of navy bean starch. Starch-Starke. 2017. https://doi.org/10.1002/star.201600305.

Information about the author:
Hrynchenko Olha Oleksiivna,
Doctor of Technical Sciences, Professor,
Professor at the Department of Food Technologies
in the Restaurant Industry
State Biotechnological University
44, Alchevskykh str., Kharkiv, 61002, Ukraine