

Методом диференційного термічного аналізу досліджувались фізико-хімічні і хімічні процеси, які відбуваються в напівфабрикаті борошняному збивному в умовах програмованої зміни температури. Проводилась якісна оцінка процесів, які відбуваються в досліджуваних зразках під час термічних перетворень.

Досліджено вплив рецептурних компонентів напівфабрикату борошняного збивного на втрати маси, швидкість перетворень і процеси дегідратації, що відбуваються за неізотермічних умов при постійній швидкості нагрівання 10 ± 1 °C/хв з нагріванням до температури 300 °C.

Підтверджено синергетичну взаємодію ксантану з желатином. Встановлено, що введення розчину ксантану в розчин желатину – основу напівфабрикату борошняного збивного, структурує і підвищує її термічну стійкість під час нагрівання. Це відбувається, вірогідно, внаслідок перерозподілу асоційованих і неасоційованих гідроксильних груп, що сприяє утворенню значної кількості міжмолекулярних водневих зв'язків.

Доведено каталітичний вплив ферменту трансглютамінази в системі желатин-ксантан імовірно на взаємодію аміногруп лізину з γ -карбоксамідною групою пов'язаних пептидним зв'язком залишків глутаміну. Цей вплив забезпечує більш високий рівень шивки макромолекул білкового каркасу і суттєво уповільнює процес дегідратації напівфабрикату борошняного збивного.

Дослідженнями встановлено мінімальні втрати адсорбційно зв'язаної вологи в напівфабрикаті борошняному збивному імовірно в наслідок підвищення ступеня зв'язаності груп -ОН з білками борошна, що зумовлює утворення міжмолекулярних водневих зв'язків із білками клейковинного комплексу.

Вивчено вплив ксантану, цукру, ферменту трансглютамінази, борошна на діапазони дегідратації, які залежать від різних форм зв'язку вологи в напівфабрикаті борошняному збивному. Визначено температурні інтервали втрати вологи з різною формою та енергією зв'язку в напівфабрикаті борошняному збивному.

Отримані результати мають практичне значення для встановлення раціональних температурних режимів випічки напівфабрикату борошняного збивного, а саме 140 ± 5 °C

Ключові слова: напівфабрикат борошняний збивний, термічний аналіз, дегідратація, неізотермічні умови, синергетична взаємодія

DETERMINING THE EFFECT OF FORMULATION COMPONENTS ON THE PHYSICAL-CHEMICAL PROCESSES IN A SEMI-FINISHED FLOUR WHIPPED PRODUCT UNDER PROGRAMMED CHANGES IN TEMPERATURE

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Received date 25.09.2019

Accepted date 04.12.2019

Published date 17.12.2019

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1. Introduction

Bread, pastry, and bakery products play an important role in human nutrition. An analysis of the food consump-

tion dynamics over the last decade has revealed that the proportion of flour-based food products in the diet structure has grown significantly and continues to increase. Flour confectionery are an integral part of the consumer basket of

people, occupying a significant segment in the confectionery market due to their high nutritional properties, food and biological value; traditionally, they belong to the products of mass consumption. Semi-finished whipped flour products include such semi-finished products as biscuit, air, air-nut, and others. The volume of production of flour confectionery accounts for more than a half of the total volume of confectionery products.

That is why efforts of specialists and scientists in the confectionery industry are aimed at the development of new technologies for high quality and consumption-safe confectionery and the extension of their range, in particular through semi-finished products.

Development of a new promising technology for the semi-finished whipped flour product with the addition to the formulation of gelatin, xanthan, and transglutaminase enzyme in order to make such confectionery as cakes, pies, while filling a significant consumer market segment, can ensure stable demand for this type of products.

Due to its functional properties, gelatin has a very wide scope of application [1]. Food gelatin is used as a gel-forming and binding material in the manufacture of a wide range of food products, gels, jelly, dairy, meat and fish products, confectionery, bakery products [2, 3]. It can be used as the emulsifier and stabilizer in the manufacture of ice cream, creams, mayonnaise, culinary products.

In cold water and in diluted acids gelatin swells, thereby absorbing water in quantities that are 10–15 times larger than its own mass. Gelatin is easy to dissolve in hot water, forming gels when cooling – this is the main property of gelatin. It is predetermined by the asymmetry of highly polymeric particles that form a solution of gelatin. The greater the asymmetry, the easier the mesh spatial frame of gels forms, whose frame's grid retains water, the more stable it gets. The dimensions and asymmetry of gelatin particles affect the structural-mechanical and physical properties of its solutions, namely: viscosity, shear stress, density, melting point and solidification temperature, weight degree of swelling.

However, the use of this hydrocolloid, which possesses a significant potential of functional and technological properties, in the technology of semi-finished whipped flour product is limited by temperature range of 30...35 °C due to the natural feature of gelatin to provide for a thermo-reversible structure. Based on this, development of a new food technology involving gelatin sets the task to scientists to find and substantiate formulation components, whose interaction with this protein complex could ensure a significant expansion of the temperature range, over which the final heat treatment of a semi-finished whipped flour product becomes possible.

Our earlier studies established, in addition to gelatin, such formulation components of the semi-finished whipped flour product as xanthan, sugar, enzyme transglutaminase, which structure and ensure the required functional properties of the semi-finished product [4]. The expediency and appropriateness of the use of these formulation components in the formulation of semi-finished whipped flour product were confirmed in the studies by domestic and foreign authors [5–10].

The most complicated phase in the technological process of manufacturing a semi-finished whipped flour product is baking it in the temperature range of 120...160 °C with the progress of physical and chemical processes that occur due to thermal effect, which necessitates studying the mechanism

of interaction among formulation ingredients in order to ensure the required moisture-retaining capacity and heat resistance. This would make it possible to reasonably approach determining the rational temperature and baking duration of a semi-finished product.

2. Literature review and problem statement

Authors of [5–9] report the results from scientific studies, which showed the prospects for the use of gelatin in the composition with xanthan and by modification with the enzyme transglutaminase in food technologies.

In recent years, significant experience has been gained in the development of scientifically reasonable food production technologies with managed processes due to the effective use of certain hydrocolloids, their mixtures with other ingredients, to stabilize technological properties of food products and their technological resistance [5, 6].

Authors of [5] demonstrated a mechanism of synergetic gelation properties of water mixtures of gelatin B and xanthan gum. It was shown that the aqueous mixtures of gelatin B and xanthan gum in the ratio (GB/XG, (0.2–2)/0.2 % by volume) ensure better gel-forming properties as compared with the solutions of their pure components at similar concentrations. The cited work provides a set of fundamental guidelines for the development of new thickeners and/or gel-forming agents based on proteins and polysaccharides for dietary or pharmaceutical applications. However, the work did not investigate the synergistic interaction between gelatin and xanthan gum and its effect on the moisture-retaining capability of the resulting gel.

An effective influence on moisture content, the addition of xanthan gum (XG) to the system gelatin-xanthan and the ratio of glucose syrup (GS): sucrose on the elastic (G') and viscous (G'') modules during gel formation and on large deformation rheological properties of thickened gels has been proven in [6]. The increase in both sample modules with the addition of XG indicates strengthening of the structural frame. All gel samples had an expressive fracture. Increasing the ratio GS:sucrose led to a decrease in the fracture stress and an increase in the fracture deformation, which testified to a more flexible polymer's grid. However, the cited paper have no results of the influence of a glucose syrup on the synergetic interactions between gelatin and xanthan gum.

Authors of [7] established the effectiveness of a positive effect on the physical and rheological characteristics of gluten-free cupcakes and dough based on millet flour with a protein isolate of chickpea in combination with the enzyme transglutaminase and xanthan. The results demonstrated that xanthan increased its specific volume and porosity and reduced hardness. It was established that the addition of enzyme transglutaminase to the formulation makes it possible to form a protein frame grid in gluten cupcakes. The results obtained make it possible to predict changes in the structural and mechanical properties of gelatin gels in the presence of the enzyme transglutaminase. The derived mathematical equations describe the processes of structure formation and make it possible to calculate a coefficient of dynamic viscosity – an important technological indicator. A mathematical model and the process of a structure formation were described at different ratios of enzyme to substrate. However, the issues that remained unexplored relate to the moisture retention capacity and heat resistance of dough

based on millet flour a result of modifying gelatin by the enzyme transglutaminase in a composition with xanthan.

The addition of transglutaminase to gelatin slightly inhibits the formation of a triple spiral. Gelatin films, modified by transglutaminase enzyme, had stronger mechanical properties than the non-modified films [8]. The highest tensile strength was observed in the gelatin films that were dried close to the gelation temperature (25 °C). It was proved that the modification by transglutaminase enzyme increased water resistance and thermostability of gelatin films by reducing the solubility in water, increasing the temperature of vitrification and a degradation temperature. However, there are the unresolved issues related to the influence of the enzyme transglutaminase on the synergetic interaction between gelatin and xanthan gum.

It is relevant for the development of new food technologies to use biotechnological techniques for obtaining products containing protein, with the assigned functional-technological properties. To this end, different methods of protein modification are used, the most effective method is enzymatic modification, which makes it possible to make changes in the properties of proteins and to influence such characteristics as gelation and the structural-mechanical properties of gels [9]. Modification of food proteins by transglutaminase leads to obtaining textured products, changes the solubility and functional-technological properties, makes it possible to obtain proteins with a high nutritional and biological value. The results obtained make it possible to predict changes in the structural and mechanical properties of gelatin gels in the presence of the enzyme transglutaminase. However, there remained the unaddressed mechanism of synergetic interaction between gelatin and xanthan gum.

Study [10] proved the effectiveness of using the transglutaminase enzyme preparation, mostly in a composition with proteins of animal and plant origin (milk, gelatin, Helios-11, different kinds of flour), in order to improve the structural-mechanical and organoleptic characteristics of gluten-free bread. It was established that this enzyme is an effective improver of the structure of pasta products made from wheat bakery flour. The action of the enzyme enhances the moisture-retaining capacity of corn dough.

Researchers in [8–10] demonstrated a mechanism of the synergetic interaction between the aqueous mixtures of gelatin B and xanthan gum leading to a change in gel-forming properties. It was proved that modification of food proteins by transglutaminase leads to obtaining textured products, which makes it possible to forecast changes in the structural and mechanical properties of gelatin gels in the presence of the enzyme transglutaminase. However, there are the unresolved issues of moisture-retaining capacity and thermal stability associated with baking pastry products, which is the most difficult phase of the technological process. During baking, physical, chemical, and colloidal changes occur in the dough, which results in the release of water that defines the character of transformation of substances occurring inside the product and ensuring the quality of finished products. Due to evaporation of moisture and decomposition of carbohydrates, protein and other organic compounds, the mass of a semi-finished whipped flour product is significantly reduced. The reason for the limited number of studies in this field could be objective difficulties associated with the absence of detailed procedures for a differential-thermal analysis of food products, perhaps a significant cost of conducting research.

The approach to the analysis of such changes, given in articles [11, 12, 14], allows us to argue that it is expedient to undertake a study that would address an analysis of the dehydration process of a semi-finished whipped flour product by the method of differential-thermal analysis.

3. The aim and objectives of the study

The aim of this study was to determine the impact of formulation components in a semi-finished whipped flour product on its thermal stability during baking. This would establish a rational temperature, ensure the necessary quality of the finished product and the minimum loss of mass during baking.

To achieve the set aim, the following tasks have been solved:

- to investigate an effect of the synergistic interaction between xanthan and gelatin on the magnitude of mass loss by a semi-finished whipped flour product;
- to explore the catalytic effect of the enzyme transglutaminase in the system gelatin-xanthan on the magnitude of mass loss by a semi-finished whipped flour product;
- to investigate mass losses by a semi-finished whipped flour product under conditions of a programmed temperature change and to define the rational temperature range of baking;
- to study the influence of formulation components in a semi-finished whipped flour product on the mechanism of moisture removal.

4. Materials and methods to study the dehydration process in a semi-finished whipped flour product using a differential-thermal analysis method

Our study objects included the formulation components for preparing a semi-finished whipped flour product, namely gelatin, as the base in a combination with xanthan, sugar, transglutaminase enzyme, and flour. Manufacturing involved nutritional additives certified for conformity and hygienic requirements. In line with the set tasks, the chemical composition of the examined samples was achieved and ensured by the use of the same kind of raw materials in each experiment. In our experimental studies, the samples with the following composition of formulation components were used: sample No. 1 – 3 g gelatin+97 g water; sample No. 2 – 3 g gelatin+0.2 g xanthan+96.8 g water; sample No. 3 – 3 g gelatin+0.2 g xanthan+30 g sugar+66.8 g water; sample No. 4 – 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water; sample No. 5 – 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water+60 g flour.

A differential-thermal analysis has been for a long time effectively used by scientists to obtain information about the kinetics of thermolysis process in a wide range of food products. All the physical and chemical processes taking place in food products during an intensive heating were studied by registering at derivatograms weight changes in a sample (TG), weight change rate (DTG), and thermal effects (DTA) at temperature (T) [11, 15].

The study was carried out in quartz crucible with an overall weight of the sample batch of 200±2 mg at a derivatograph in the “Paulik Erdey” system (Hungary) in the air

environment of the derivatograph's furnace at a constant heating rate of 10 ± 1 °C/min to a temperature of 300 °C, which is 160 °C higher than the temperature of baking. The reference used was Al_2O_3 baked to 2,800 °C [11, 12].

Considering the reproducibility accuracy of derivatograms from a 4-channel derivatograph's recorder, the studies were repeated at least 3 times. The objective judgement on the degree of reliability of the acquired data was verified by mathematically treating the results using the standard software package Excel (2016). The result accepted was the arithmetic mean of results from the analysis of derivatograms, data discrepancies in which did not exceed 1%. Derivatogram's curves were decoded in line with known procedures [16].

5. Results of research into the influence of formulation components on moisture loss by the model system of a semi-finished whipped flour product

5.1. Studying the influence of synergetic interaction between xanthan and gelatin on the magnitude of mass loss by the semi-finished product

In order to determine the dynamics in moisture loss, which has various forms of binding to protein [14–17] during heat treatment as the base of the model system with different content of formulation ingredients and in the model system of the semi-finished whipped flour product, experimental curves were used to estimate the mass of kinematically unequal water molecules by a thermogravimetry method (DTG) and by a differential-thermal analysis (DTA) under non-isothermal conditions (Fig. 1–3).

It was established while studying the impact of formulation ingredients on moisture-retaining capacity of the model system of the semi-finished whipped flour product that the process of decomposition of all samples occurs differently.

Decomposition of the first sample (gelatin) and the second sample (gelatin+xanthan) (Fig. 1, *a, b*) occurred in two stages in temperature ranges, respectively, 1 – 80 ± 3 °C, 2 – 108 ± 3 °C, and 1 – 80 ± 3 °C, 2 – 114 ± 3 °C.

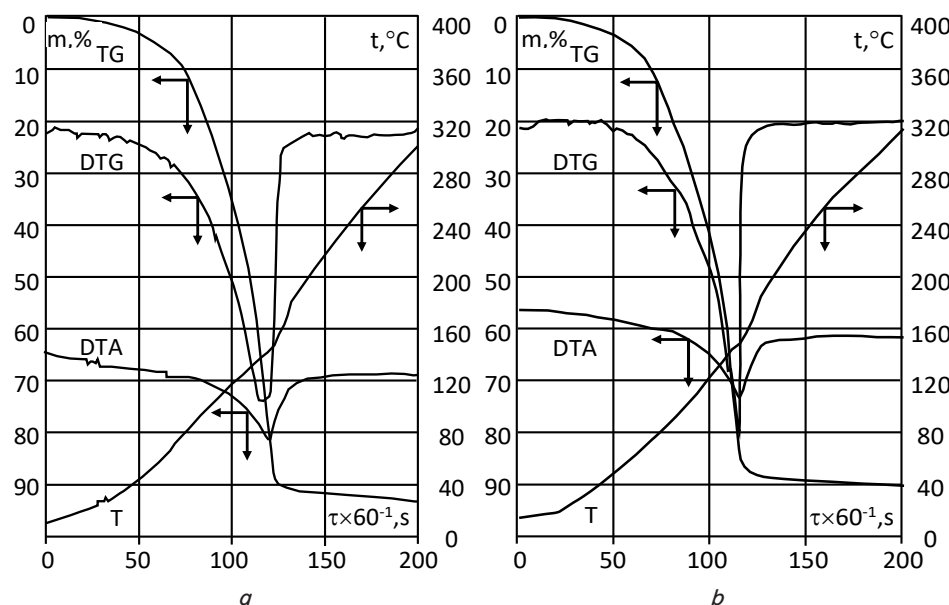


Fig. 1. Derivatograms of the base of the model system of a semi-finished whipped product containing: *a* – gelatin 3 g and water 97 g; *b* – gelatin 3 g, xanthan 0.2 g, water 96.8 g

The DTA curves (Fig. 1, *a, b*) registered endothermic reactions that occur with an intense absorption of heat [14–17]. Each stage characterizes the process of a mass loss, which occurs in the base of the model system and in the model system of a semi-finished whipped flour product under the influence of temperature.

The first stage characterizes the onset of a process to remove immobilizing moisture, which is kept by the frame of a semi-finished whipped flour product, the second one characterizes the process of intensive removal of adsorption and osmotic bound moisture, the third one – the completion of the process of intense moisture removal with a partial removal of chemically bound moisture.

The character of TG curves in derivatograms (Fig. 1, *a, b*) demonstrates that in the temperature range 35...80 °C (range I – onset of polymorphic transformations in protein) there is an intensive removal of free non-bound or mechanically bound water. The losses of water by the base of the model system of a semi-finished whipped flour product (samples 1, 2) are, respectively, 12.5 ± 0.5 %; 10.0 ± 0.3 %.

In the temperature range 80...120 °C (range II – the onset of heat treatment) there occurs the removal of mechanically bound water, which is found in cells of protein-containing components, and the osmotically bound water during a whipping process and when forming a dough semi-finished product. The losses of water (samples 1, 2) are, respectively, 65.5 ± 0.2 %; 32.0 ± 0.2 %. The highest hydration capacity is demonstrated by the model system containing xanthan (sample 2).

In the temperature range 120...160 °C (range III – the main range of heat treatment) the water losses (samples 1, 2) are, respectively, 95.5 ± 0.2 %; 80.0 ± 0.2 %. The decrease in moisture loss by 15.5 % (sample 2) occurs as a consequence of synergetic interaction between xanthan and gelatin, obviously due to the redistribution of associated and non-associated hydroxyl groups, which contributes to the formation of a significant number of intermolecular hydrogen bonds.

5.2. Studying the catalytic effect of transglutaminase enzyme in the system gelatin-xanthan system on the magnitude of mass losses by a semi-finished product

The DTA curves (Fig. 2, *a*) registered the endothermic reactions occurring with an intense absorption of heat. Along the DTA curves (Fig. 2, *b*) the process is not accompanied by thermal reactions [14–17].

Decomposition of the third sample (gelatin+xanthan+sugar) and the fourth sample (gelatin+xanthan+sugar+transglutaminase) (Fig. 2, *a, b*) occurs in three stages in temperature ranges 1 – 85 ± 3 °C, 2 – 120 ± 3 °C, 3 – 124 ± 3 °C.

Our analysis of TG curves in the derivatograms (Fig. 2, *a, b*) established that in the temperature range 35...80 °C (range I – inset of polymorphic

transformations in protein) the water losses by the base of the model system of a semi-finished whipped flour product (samples 3, 4) are, respectively, $8.5 \pm 0.2\%$; $6.5 \pm 0.2\%$.

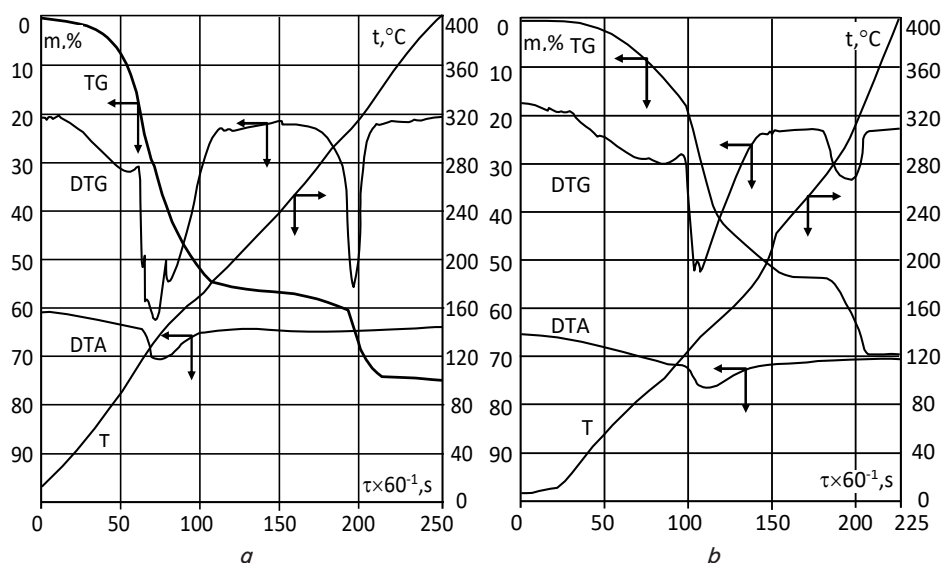


Fig. 2. Derivatograms of the base of the model system of a semi-finished whipped product containing: *a* – 3 g gelatin+0.2 g xanthan+30 g sugar+66.8 g water; *b* – 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water

In the temperature range $80 \dots 120^\circ\text{C}$ (range II – the onset of heat treatment) the water losses (samples 3, 4) are, respectively, $25.5 \pm 0.2\%$; $23.0 \pm 0.2\%$.

In the temperature range $120 \dots 160^\circ\text{C}$ (range III – the main range of heat treatment) the water losses (samples 3, 4) are, respectively, $58.5 \pm 0.2\%$; $49.0 \pm 0.2\%$. That is, introducing to the base of the model system of a semi-finished whipped flour product of sugar and transglutaminase enzyme contributes to an increase in hydration capacity by, respectively, $21.5 \pm 0.2\%$ and $31.0 \pm 0.2\%$ relative to sample 2 (the system gelatin–xanthan). The highest hydration capacity is demonstrated by the model system containing the enzyme transglutaminase (sample 4).

Our analysis of TG curves in the derivatograms of a semi-finished whipped flour product (Fig. 2, *a*, *b*) established that the reduction of moisture loss is presumably due to the catalytic effect exerted by the enzyme transglutaminase in the system gelatin–xanthan on the interaction between the amino groups of lysine and the γ -carboxamide group of glutamine residues bound through a peptide bond.

5. 3. Studying the weight loss by a semi-finished whipped flour product under conditions of the programmed temperature change and determining the rational temperature range for baking

In the DTA curves (Fig. 3) the process of the mass loss by the model system of a semi-finished whipped flour product is not accompanied by thermal reactions [14–16]. Decomposition of the fifth sample (gelatin+xanthan+sugar+transglutaminase+flour) occurs in three stages in temperature ranges 1– $100 \pm 3^\circ\text{C}$, 2 – $140 \pm 3^\circ\text{C}$, 3 – $200 \pm 3^\circ\text{C}$.

Our analysis of TG curves in the derivatogram (Fig. 3) established that among all the examined samples of the model system of a semi-finished whipped flour product the loss of water is the lowest in sample 5. In the temperature range

$35 \dots 80^\circ\text{C}$ (range I – onset of polymorphic transformations in protein) the water loss is $5.0 \pm 0.1\%$.

In the temperature range $80 \dots 120^\circ\text{C}$ (range II – the onset of heat treatment) the water loss (sample 5) is $21.0 \pm 0.2\%$.

In the temperature range $120 \dots 160^\circ\text{C}$ (range III – the main range of heat treatment – baking) the water loss (sample 5) is $41.0 \pm 0.2\%$. That is, adding to the model system of a semi-finished whipped product the flour in a corresponding concentration contributes to a significant reduction of moisture loss, presumably due to an increase in the binding degree of -OH groups to the proteins in flour, which predetermines the formation of intermolecular hydrogen bonds with the proteins of a glutinous complex. In addition, the temperature of $140 \pm 5^\circ\text{C}$, which is within a given temperature range, can be considered as rational for baking a semi-finished whipped flour product.

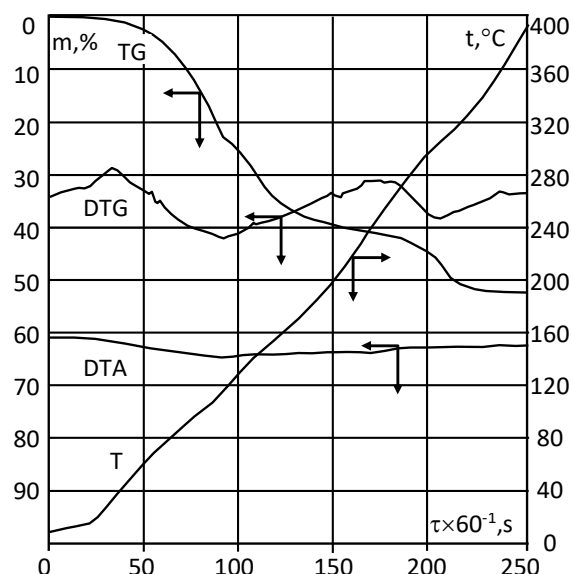


Fig. 3. Derivatogram of the model system of a semi-finished whipped product containing: 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water+60 g flour

5. 4. Studying the influence of formulation components in a semi-finished whipped flour product on the mechanism of moisture removal

To obtain data on the mechanism of moisture removal, we calculated, based on the TG curve, the degree of change in mass Δ (Fig. 4) and built a dependence $|\lg \Delta$ on the magnitude of a reverse temperature $1,000/\text{K}$ (Fig. 5) over

interval 328...378 K, because this is the range where the dehydration processes in the model system of a semi-finished whipped flour product proceed most intensively, which is evidenced by the endoeffects in the derivatogram charts (Fig. 1, 2) [14, 15].

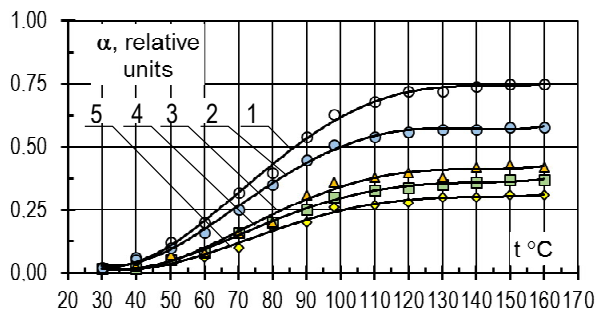


Fig. 4. Dependence of the degree of mass changes in the model system of a semi-finished whipped product on temperature at the following content of formulation components:

- 1 – gelatin 3 g and 97 g water;
- 2 – gelatin 3 g, xanthan 0.2 g, and 96.8 g water;
- 3 – 3 g gelatin+0.2 g xanthan+30 g sugar+66.8 g water;
- 4 – 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water;
- 5 – 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water+60 g flour

It is known that the rate of mass loss (a DTG curve) corresponds to the process of dehydration, which is why we applied this factor in the heat treatment (baking) of a semi-finished whipped product used in order to obtain the dependence of mass change on temperature. To this end, we derived, on the TG curve, at constant temperature intervals of 10 °C, a change of mass Dm_1 in the sample of a semi-finished whipped flour product, which corresponds to the amount of moisture that evaporated under the influence of temperature [11, 12].

The degree of change in mass a (Fig. 4) was calculated as the ratio Dm_1 to the total amount of moisture contained in the base of the model system (samples 1–4) and in the model system of a semi-finished whipped flour product w (sample 5) and removed at the end of the dehydration process (the TG curve).

The TG curves obtained in the a – t coordinates (Fig. 4) take the S-shaped form, which characterizes complex forms of interaction between water and dry substances in the base and the model system of a semi-finished whipped flour product and implies a difference in the rate of water release along different sections of the curves. Thus, the curves of dependences for a change in the mass of the model system of a semi-finished whipped flour product on temperature make it possible to study the energy of water activation, the kinetics of non-equal forms in moisture binding, and reflect the different rate of dehydration of the finished product [11, 14].

At the first stage, at a temperature of 303...323 K (Fig. 5, section AB), there is the removal of “free” or mechanically bound (capillary) moisture, which has a low binding energy with the base’s protein and the semi-finished whipped flour product. First, the water is released that forms a structural grid of water molecules interconnected by hydrogen bonds. In this case, the desorption of capillary water is characterized by lower activation energy values compared with water, which is released at the second stage of the process [11].

At the second stage (section BC), during heating at a temperature of 323...378 K the share of osmotically and immobilize-bound moisture, which is retained in the closed cells of protein micelles in a semi-finished whipped product, is released as a result of deployment of their polypeptide chains as a result of disruption of their micellar and hydrophobic interactions between proteins and carbohydrates and water [12, 14].

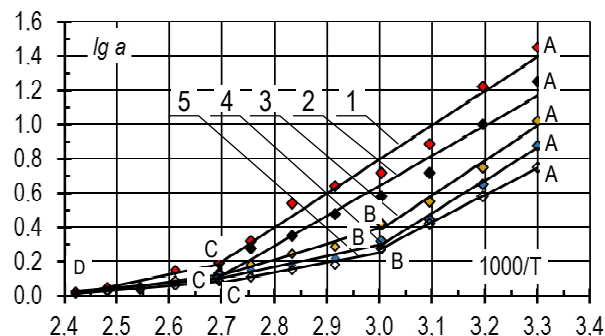


Fig. 5. Dependence of logarithm of a mass change degree in the model system of a semi-finished whipped product on temperature at the following content of formulation components: 1 – gelatin 3 g and 97 g water; 2 – gelatin 3 g, xanthan 0.2 g and 96.8 g water; 3 – 3 g gelatin+0.2 g xanthan+30 g sugar+66.8 g water; 4 – 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water; 5 – 3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water+60 g of flour

In the temperature range 378...416 K at the third stage (section CD) there begins the release of a portion – 41 % of the weakly-bound adsorption moisture of the polymolecular layers within the particles of the model system of a semi-finished whipped product with the release of gaseous fractions. The water that is being released forms several next layers of molecules, more firmly bound to protein in the model system of a semi-finished whipped flour product.

6. Discussion of results from studying the effect of formulation components on moisture loss by the model system of a semi-finished whipped flour product

The results from our thermal analysis of samples of the semi-finished whipped flour product are explained by the synergetic interaction between xanthan and gelatin [5, 6] and by the enzyme modification of food proteins [7–9], which ensured the formation of the mesh frame and, as a consequence, the increased moisture-retaining capacity and the improved thermal stability.

The thermal analysis of a semi-finished whipped flour product, stabilized by the exopolysaccharic xanthan and the enzyme transglutaminase, is one of the fast enough and most precise methods of laboratory testing. This method makes it possible to determine the overall moisture loss, determine the forms of moisture, moisture binding energy, as well as thermal effects occurring due to the physical and chemical transformations. In combination with other methods, thermal analysis is suitable for a relatively quick and reproducible characteristic of structural changes and state transitions occurring in a semi-finished product due to thermal impact [11, 15–19].

The results from our thermogravimetric study of samples of the model system of a semi-finished whipped flour product have clearly confirmed the appropriateness of using gelatin as a base in a combination with xanthan and the enzyme preparation transglutaminase [8–10].

It was established in the study of efficiency of the integrated interaction between xanthan and gelatin, the base of the model system of a semi-finished whipped flour product, that such a modified system is better structured, probably as a consequence of the redistribution of the associated and non-associated hydroxyl groups, which contributes to the formation of a large number of inter-molecular hydrogen bonds and thus improves their moisture-retaining capacity by $15.5 \pm 0.2\%$ and increases its thermal stability during heating. Researchers [5, 6] confirmed the synergistic effect of the pair of gel-formers xanthan and gelatin and their rational use in complex gel-based systems.

We have experimentally confirmed the catalytic effect of transglutaminase in the system gelatin-xanthan likely on the interaction between the amino groups of lysine and a γ -carboxamide group of glutamine residues bound through peptide bonds, which provides for a higher level of crosslinking the macromolecules in a protein frame, and, as a consequence, it significantly slows down the dehydration process of the base of the model system of a semi-finished whipped flour product, by $31.0 \pm 0.2\%$. These results are consistent with the experimental data by authors of [7–10] who also proved the effectiveness of using the enzyme transglutaminase mostly in the composition with proteins of animal and plant origin (gelatin, different types of flour) to improve the structural and mechanical characteristics and the moisture-retaining capacity of flour dough.

The minimum losses of adsorption-bound moisture in the model system were established, probably as a consequence of increasing the degree of binding the $-\text{OH}$ groups with flour proteins, which predetermines the formation of intermolecular hydrogen bonds with the proteins from a glutinous complex. Overall mass losses when the model system of a semi-finished whipped flour product is heated to $160 \pm 5^\circ\text{C}$ amount to $41.0 \pm 0.2\%$.

The thermoanalytic study helped investigate the complex effect of xanthan, sugar, transglutaminase enzyme, flour, on the ranges of dehydration, which depend on various forms of moisture binding in a semi-finished whipped product. We have determined temperature intervals of moisture loss by a semi-finished whipped product under different forms and binding energy.

Thermographic studies of food products require certain experience and knowledge for decoding, for treating derivatograms and for construction of secondary graphs of the degree of mass changes, which may complicate their application in industrial settings. Therefore, when enterprises set out to devise new technologies, it is better for them to use a modern derivatograph, the TGA/DSC1 model, which is operated by a

computer. This ensures that the results are acquired and data processed instantaneously. In addition, the information about a sample weight change (TGA) is supplemented in an automated mode with data on the thermal processes occurring during physical-chemical transformations in an examined sample – a differential-scanning calorimetry (DSC) signal.

7. Conclusions

1. Our thermal analysis of the samples of a semi-finished whipped flour product has confirmed the synergetic interaction between xanthan and gelatin. This interaction contributes to the structuring of the base and increases its thermal stability during heating, presumably due to the redistribution of associated and non-associated hydroxyl groups, which leads to the formation of a large number of inter-molecular hydrogen bonds and is confirmed by the losses of mass in the base of a semi-finished whipped flour product. The total mass losses of sample number 1 (3 g gelatin+97 g water) amounted to $95.5 \pm 0.2\%$, and when introducing xanthan to sample number 2 (3 g gelatin+0.2 g xanthan+96.8 g water) they decreased by $15.5 \pm 0.2\%$.

2. We have proven the catalytic effect of transglutaminase enzyme in the system gelatin-xanthan probably on the interaction between the amino groups of lysine and a γ -carboxamide group of glutamine residues bound via a peptide bond, which provides for a higher level of crosslinking the macromolecules in a protein frame and substantially slows down the dehydration process of the base of the model system of a semi-finished whipped flour product. The losses of moisture by sample number 4 (3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water) amounted to $49.0 \pm 0.2\%$, which is 46.5 % less than those in the first sample.

3. It has been established that under the influence of the enzyme transglutaminase the wheat flour water-retaining capacity is considerably increased while its thermal stability grows. The losses of moisture by a semi-finished whipped flour product at the following content of formulation components, sample number 5 (3 g gelatin+0.2 g xanthan+0.2 g transglutaminase+30 g sugar+66.6 g water+60 g flour), are the smallest and are $41.0 \pm 0.2\%$ in the temperature range $120...160^\circ\text{C}$. Thus, it is recommended, given such a composition of formulation components in a semi-finished whipped flour product, to use the temperature of $140 \pm 5^\circ\text{C}$ for baking.

4. It has been proven that the model system of a semi-finished whipped flour product has complex forms of interaction between water and dry substances and implies different forms of moisture binding, which would contribute to slowing down the product dehydration rate during baking. We have defined temperature intervals of moisture loss with different forms and binding energy by a semi-finished whipped flour product.

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