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TECHNOLOGY OF THERMOSTABLE AND FROZEN FILLINGS USING DAIRY RAW MATERIALS AND SESAME SEEDS CONCENTRATE

Monograph

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The monograph contains concentrated and systematic scientific information on the use of dairy raw materials and sesame seeds concentrate for the production of thermostable dairy-containing fillings in the restaurant industry, represented by text form, technological calculations, drawings, schemes, tables and is intended for teachers, postgraduate students, students engaged in scientific work.

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CONTENT

List of abbreviations and symbols

MHA – moisture-holding ability
AHF – ability to hold fat
SMP – skimmed milk powder
SSC – sesame seeds concentrate
TI – technological instruction
TF – thermostable filling
TS U – Technical specifications of Ukraine
NMR – nuclear magnetic resonance

Introduction

In the modern food market more and more strong position is taken by the baked products with fillings. Producers are constantly updating their assortment, mainly due to use of various dough improvers, and fillings mostly leave traditional: jam, confiture and also fillings made on the basis of fruit puree and sugar, a dairy, fondant and fatty basis. Such fillings, on condition of their introduction in the crude dough, are negatively affected by temperature during baking and lose much of their primary organoleptic, nutritional and technological properties and become excessively fluid. Therefore, for preservation of quality indicators at the constant level, the fillings entered into the dough products must be heat-resistant, that is, do not lose shape during temperature about 200...230 °C during (10...15) × 60 s. Widespread got heat-resistant fillings based on fruit, vegetable, berry and fruit-berry raw materials . However, due to boiling, these fillings change the structural and mechanical properties. Milk and milk-containing fillings characteriz higher nutritional and biological value. By monitoring the current market of heat-resistant fillings, regardless of their basis, we can conclude that the conditions of storage of these products offered by manufacturers are very different. But most manufacturers offer the following storage conditions: at temperatures from 0 to 25 °C and relative humidity not higher than 75%, heat-resistant fillings are stored for up to 6 months. Obviously, such a wide temperature range for a sufficiently long shelf life of the filling will lead to significant negative changes in their quality characteristics. In this regard, it is expedient to pay attention to such a perspective way oof storage of foodstuff as freezing.

Heat-resistant properties to the fillers can provide pectin. In spite of the fact that heat-resistant properties of products with pectin rather high, for receiving a product with steady physical and chemical properties, in particular with low content of free moisture, it is expediently to use starch, which begins to bind the free moisture when heated. Considering relevance of a problem of complex and waste-free use of agroresources and creation of a product with the combined animal-plant composition, it is expedient to use in the technology of heat-resistant fillings of plant protein concentrates of oil-bearing crops. The most perspective way of processing protein oil raw materials is cold pressing, which allows to obtain both products (oil and concentrate) with a high content of technologically unchanged nutrients. A special place among plant protein oil crops, owing to its high protein content (about 20 %), fat (within 48 %), calcium, magnesium, potassium, phosphorus, iron, a number of fat-soluble vitamins and antioxidants, is sesame. Thus, the processing of sesame into concentrate is a perspective scientific direction for obtaining a plant protein supplement with high nutritional and biological value.

The development of combined technologies dairy products, in particular emulsion, structured and pasty snacks, desserts, cheeses and cheese products with using of milk and plant components, is a subject of particular attention of domestic and foreign specialists. A significant contribution to the development of these technologies was made by R.Yu. Pavlyuk, V.V. Pogarskaya, N.P. Zakharova, F.V. Pertsevoy, O.O. Grinchenko, G.B. Rudavska, S.S. Gulyaev-Zaitsev, V.A. Tutelyan and other scientists. However, systematic studies aimed at obtaining the frozen thermostable filling using hydrocolloids, as well as dairy raw material in combination with plant protein concentrates of oilseeds, have not been found in the literature.

Given the above, a prespective direction for the development of filling technology for confectionery and culinary products is the development of new science-based technology and recipe of thermostable filling with combined composition, which is achieved by using dairy raw materials and concentrate of sesame seeds, the thermal resistance of which is due to the combined use of the properties of pectin and starch, high nutritional and biological value - the introduction into the recipe composition of sesame seeds concentrate, and the constancy of physical and chemical properties - the use of freezing.

In connection with the above, studying the technologies of dairy-containing foodstuffs with the combined compounding composition and development of a new generation of foodstuffs, taking into account the current trends and changes that are presently present, are relevant and timely.

The monograph contains materials which include characteristic and the review of the modern ways of receiving the combined dairy products and receiving with their use of new culinary products.

The first chapter provides an analysis of consumer, technological and physico-chemical aspects of production of a dairy-containing thermostable fillings; the use of thickeners, structure-forming agents and plant protein products in the technology of dairy-containing thermostable fillings is substantiated; the expediency of influence of the freezing process on the quality of dairy-containing thermostable fillings is shown.

The second chapter provides a scientific justification of the technology of milk-containing thermostable fillings using dairy raw materials and sesame seeds concentrate. Functional-technological properties of hydrocolloids, protein concentrates of oilseeds, rational ratio and influence of recipe components on the duration of structure formation, thermal resistance and strength of milk-containing fillings are considered in detail.

The third chapter presents materials that are devoted to the development of technology of dairy-containing thermostable filling with use in the recipe of dairy raw materials and sesame seeds concentrate; the prescription composition and technological process of the offered products have been developed; the chemical composition, microbiological and physico-chemical parameters, its rheological properties and quality quality were investigated.

The group of authors hopes that this work will be useful to engineers-technologists working in the food industry and institutions of restaurant economy, postgraduate students, teachers and students who want to deepen their knowledge of this scientific direction.

1 Analysis of production technologies of thermostable dairy-containing fillings, features of application of plant protein products and prospects of freezing

1.1 Prospects of production, analysis of consumer, technological and physicochemical aspects of production of thermostable fillings

1.1.1 Features of assortment formation and substantiation of recipe components of thermostable fillings

Today, leading confectionery enterprises produce not only a wide range of finished products, but also are characterized by the production of semi-finished products, in particular fillings that have high consumer demand, as they are able to meet the various requirements of potential consumers. They found their use in the baking and dairy industries mainly in culinary and confectionery products. Depending on the components of the recipe composition, the fillings are able to give a variety of flavors, textural properties, nutritional and biological value, expanding the range of products.

Confectionery fillings, due to the combination of their properties, can be grouped and classified (Table 1.1). In the context of this classification, fillings are complex multi-component systems consisting of different types of raw materials. Their physicochemical properties are due to a certain ratio of the mass fraction of free and bound moisture, the absence of sucrose crystallization, and regulated rheological parameters. These indicators directly affect the shelf life of the fillings, which has a different duration (usually not less than three months).

The fillings of the first group are fillings, which include mono-, disaccharides and substances that act as anti-crystallizers. They include: treacle, various types of invert syrup, dextrins and other substances that contribute to the viscosity of the system.

The fillings of the second group belong to suspensions. They are based on: sucrose in the form of sugar, powdered sugar and other sugars (glucose, fructose, etc.), nuts (grit of different sizes and extent of thermal treatment), dry products - milk and cocoa, fat component, in the role of which is used not only milk and confectionery fats, but also oil of cocoa, coconut, palm, palm kernel and others.

Table 1.1

Classification of confectionery fillings

Group fillings	Name of filling	Basic processes of fillings technology		Characteristics of fillings		
		technological	physico-chemical	Sugar condition	Volume fraction of solids, %	Resistance to temperature influence*
First	Fruit and berry	Mixing and boiling	Homogenization and concentration	Amorphous in the form of solution	67,0–84,0	T, C
	Honey			The same	84,0– 86,0	T
	Liqueur			Amorphous in the form of solution / amorphous crystalline	69,0–86,0	NT
	Dairy			The same	83,0–88,0	NT
	«Soft caramel»			Amorphous in the form of solution	78,0–82,0	C
Second	Marzipan	Grinding and rubbing	Increasing dispersion and homogenization	Crystalline, in suspension form	90,0–94,0	T, C
	Chocolate				97,1–99,1	NT, C
	Chocolate-nut				96,1–99,0	NT, C
	Butter and nut				93,4–98,9	T, C
	Butter and sugar				96,7–99,8	NT, C
Third	Jelly	Gelling and maturation	Structure formation	Amorphous in the form of solution	67,0–84,0	NT
Fourth	Fondant	Churning, cooling	Crystallization	Amorphous and crystalline at the same time	84,1–90,4	NT
	Cream	Churning-stabilization	Emulsification	Amorphous in the form of solution	88,0–99,2	NT, C
	Churned	Churning-maturation	Foaming	The same	76,0–88,0	NT

Note: T – thermostable, NT – non thermostable, C – cryostable.

The third group is jelly fillings. The peculiarity of their technology is the boiling of sucrose syrup containing sucrose in solution, with the addition of hydrocolloids (agar, agarid, pectin, furzelaran, modified starch, etc.) and fruit and berry raw materials. A necessary technological operation is a structure formation that depends on the amount of hydrocolloid, its type and technological parameters (temperature, time, acidity of the medium and nature of the components).

The fourth group includes fillings of fondant, cream and churned with a joint operation - churning. The fondant fillings are characterized by fine-crystalline mass, where sucrose is in the form of crystals and solution. Their quality depends on the technological parameters (churning speed, cooling temperature, etc.), the ratio of sucrose and anticrystallizer. Cream fillings are emulsions with soluble sucrose. Their quality is greatly influenced by the ratio of water and fat phases, as well as the properties of the emulsion.

The peculiarity of churned fillings is due to the presence of foaming agent. Foaming depends on the amount and type of foaming agent, as well as the technological conditions of production [15; 91; 100].

Modern confectionery production, to meet the complex of the above requirements made recently, requires the creation new or upgrading of traditional production technologies taking into account consumer demand. To the fillings which are most demanded are fillings with thermal resistant structure.

Thermostable filling is a product made on the basis of whole or ground to a puree state of raw materials, which has a jelly consistency due to the introduction of special structure-forming components (e.g., pectins), consistency stabilizers and other ingredients [58; 220]. It is considered thermostable filling if it is able to retain its functional-technological and physicochemical properties (shape, texture, volume fraction of solids, etc.) under normal baking conditions (convection method (200…230)^{o} C, (10…15)×60 s) [59; 72; 133; 220].

In general, the filligs subject to high temperature influences are divided into three groups: thermostable filling ; fillings with limited thermostable properties; fillings which have no thermostable properties [90; 210]. The melting temperature of the thermostable filling is above 200 °C with at distribution from 200 °C on the surface of the filling and up to 115 °C inside. Its shape should not boil and form bubbles on the surface of the so-called "craters" [125; 220]. The melting temperature of the filling with limited thermostable properties is in the range from 115 to 200 °C with a similar temperature distribution during thermal exposure. Its shape changes slightly, the surface melts and a shiny layer is formed. The melting point of the filling, which has no thermostable properties, is lower than 115 °C. Under conditions of temperature influence of about 200 °C, it melts and completely changes its shape [71]. Thermostable fillings are widely used in the confectionery industry, especially in flour products, which make up a large part of the confectionery production volume and have a wide range that satisfies the diverse range of consumer needs [39; 90; 161].

There are a number of enterprises in Ukraine today, which for many years have been representatives of domestic and foreign producers of raw materials for our country's confectionery industry. Their customers include pastry shops, retailers and hospitality industry representatives «HoReCa» (Hotel, Restaurant, Cafe/Catering): “Master Martini” (Italy), “Puratos” (Belgium), “Modecor” (Italy), “De Cecco” (Italy), “Alderman” (Germany) and others. However, the vast majority of such businesses and companies offer thermostable fillings made from fruit raw materials, rarely dairy [46; 64; 221].

Presenters of thermostable confectionery fillings, which are nowadays widely represented in the food market of Ukraine, are distributor-production enterprises that not only produce their own products, but also represent well-known brands that are in high demand among consumers. Thus, the following has been identified through the monitoring of the food consumer market. Known manufacturers of thermostable fillings based on fruit raw materials are the following distributor-production enterprises: "Fruit Ex" (Kyiv region, Trebukhov village, Ukraine), "Nadiya-V PP" (Vinnytsia region, Luka-Meleshkovskaya village, Ukraine), "Zinto" (Cherkasy, Ukraine), "Petrikov Cannery" (Dnipropetrovsk region, Petrikovka village, Ukraine), "Nadiinyi partner" (Zaporizhzhia, Ukraine), "Compass Dessert" (Voronezh, Russia), "Bargus Trade" (St. Petersburg, Russian Federation), "Bery Style" (Korolev, Russian Federation), "Linii Vkusa" (Ufa, Republic of Bashkortostan), "Soyuzsnab" (Krasnodar, Russian Federation), "Pacific" (Vladivostok, Russian Federation), "Berta" (Stavropol, Russian

Federation). Manufacturers of thermostable fillings made from dairy raw materials are: «"Nadiinyi partner" (Zaporizhzhia, Ukraine), "Zinto" (Cherkasy, Ukraine), BMB Blend (Kyiv, Ukraine), "Compass Dessert" (Voronezh, Russia), "Bargus Trade" (St. Petersburg, Russian Federation), "Linii Vkusa" (Ufa, Republic of Bashkortostan), "Soyuzsnab" (Krasnodar, Russian Federation), "Berta" (Stavropol, Russian Federation), as well as a number of Italian companies that are limited to the Ukrainian market («Irca», «Italcanditi», «Salumificio Su Sirboni», «Novacart», «Ferrero SpA» etc.).

According to the carried-out monitoring of the recipe composition of traditional thermostable confectionery fillings, which are currently presented on the consumer market of Ukraine, revealed that the recipe ingredients are varied and have certain functional features, however it is difficult to make their accurate differentiation. Thus, the traditional recipe composition of thermostable confectionery fillings may include: fruit puree, jam, fruit slices, sugar (sugar substitutes and sweeteners), thickeners or system stabilizers (e.g., wheat flour, starch, pectin, etc.), flavorings, dyes, citric acid, and preservatives [42; 84; 86; 113; 121; 206; 227].

An important functional property of thermostable confectionery fillings is their ability to structure formation. And as the structure-forming act as their own pectins of fruit raw materials, and pectins added as a dietary supplement. A rather significant contribution to the study of the properties of hydrocolloids was made by the scientific school of Doctor of Technical Sciences, Professor, Academician of the International Cold Academy, Excellence in Education of Ukraine Pertsevyi F.V. - «Scientific substantiation and development of technologies of modified drag-forming agents» and Doctor of Technical Sciences, Professor, Academician of the International Cold Academy, Excellence in Education of Ukraine, laureate of the State Prize of Ukraine in the field of science and technology Pyvovarov P.P. "Scientific fundamentals of technology of the re-structured products received by monotropic gel formation".

The following scientists have made a significant contribution to the development of the confectionery industry in the context of thermostable fillings:

− Koretska I.L., Kiryanova G.A., who have developed a jelly thermostable filling. Its recipe includes sugar, pectin, citric acid, molasses and gum. The prepared recipe components are mixed and boiled, adding gum and pectin to the mass fraction of solids 67-69%, then added citric acid, stirred and poured in capacity. The resulting filling has a thermostable properties due to the adding of pectin and gum, which belongs to the group of heteropolysaccharides and is a natural thickener-stabilizer. Its use together with pectin leads to a significant reduction of syneresis and less intense color change of the finished product, as well as improvement of the structural and mechanical properties of the finished product [141; 142; 144; 145].

− Kropyvnytska I.O., Obolkina V.I., Yovbak U.S., Kambulova Yu. V., who developed thermostable filling for flour confectionery, which includes: hydrolysed carrot puree, white sugar, starch molasses, pectin apple with an esterification rate of 31-36%, citric acid and calcium citrate, which are used to form the gelatinous structure of low-esterified apple pectin. It is characterized by the highest activity and high efficiency for complexing with pectin among all calcium salts [146; 149].

− Cherevko O.I. and other scientists of Kharkiv State University of Food Technology and Trade developed thermostable fillings from vegetables and pumpkin jam, enriched with heme iron, thermostable fillings from fruit and apple jam and dried fruits. The recipe composition of these fillings contains fruit base, diet supplement "Hemovital" and jerusalem artichoke powder . The technological process of production consists in the preparation of fruit and vegetable raw materials, the preparation of the recipe mixture by mixing pre-prepared raw materials with sugar and boiling. The filling has a sweet taste with a light acidity, a plastic and thick consistency with the color corresponding raw material used; it can be used in confectionery [135; 136; 138; 206; 227].

From stated above follows that the fillings acquire thermostable properties due to the presence in their composition of a rational concentration of one or more structure-forming agents, which improve their functional and technological properties due to the synergistic effect on each other. Of course, a number of thermostable fruit-based toppings do not contain protein. Therefore, another quite interesting by assortment and chemical composition, in particular the presence of protein, is a separate direction of development of the confectionery industry - the production of thermostable dairy-containing fillings.

1.1.2 Features of production technologies of thermostable dairy-containing fillings

The modern assortment of dairy-containing thermostable fillings include fillings for confectionery products, which are used as fillers and surface finishers of flour confectionery products with fillings and other food products. Such fillings are characterized by stable physicochemical and organoleptic properties at influence of high and low temperatures. These include: thermostable fillings "Souffle" made according to TS 9142-003-72446492-09, "Boiled condensed milk" thermo 3000 - according to TS 9129-002-87168165-11, fillings made according to TS 9129-023 -52176062-2009, which assortment number is as follows: "Boiled condensed milk"; "Butter cream"; "Cream cheese"; "Cottage cheese cream"; "Cream Brulee"; "Vanilla cream"; "Cream-chocolate".

An essential component of the formulation of these thermostable dairy-containing fillings is stabilizing systems, which are mainly pectins, caragines, alginates, starches and other hydrocolloids. The choice of hydrocolloids or a composition of them depends on their ability to impart the required consistency, certain physicochemical and structural-mechanical properties to the finished filling. In this case, the obligatory recipe component is dairy raw material of different production methods and physicochemical properties, which gives the finished product characteristic organoleptic properties [61, 73; 106; 122; 164; 169].

Considering given above, the characteristic of thermostable fillings of fruit and dairy-containing ones, we note that their main feature lies in the recipe composition and to some extent in the duration and expenses of raw materials during their production. Thus, thermostable fruit fillings are produced by boiling fruit raw materials in sugar syrup to a certain amount of solids. Thermostable dairy-containing fillings are made by mixing all of the recipe components with subsequent heat treatment, which continues until the filling reaches the necessary amount of solids,which characteristic of its certain type.

The technological processes of production of thermostable fruit and dairy-containing fillings are somewhat different. The technological process of production of thermostable fruit fillings is characterized by significant raw material costs and long-term influence of high-temperature modes [15; 43; 78; 98; 100; 121; 255]. It should be noted that during the long-term heat treatment of fruit raw materials there is a partial inversion of sucrose, hydrolysis of pectin substances and reducing of nutritional value, as well as loss of vitamins, flavors and formation of difficult-to-digest sugar aromatic complexes in products [98; 121; 223]. Thus, the considered traditional thermostable fillings do not have high functional and technological parameters that would meet the modern requirements of manufacturers who seek to reduce the technological process of production. That is why thermostable dairy-containing fillings have become quite widespread recently.

However, a characteristic feature and at the same time a certain disadvantage of dairy-containing fillings is the impact on their main raw material base of seasonality, mainly due to the decrease in the number of dairy animals, which has led to a decrease in milk yields and its physical organization. Therefore, the relevance is acquired of using skimmed milk powder because it is a valuable raw material with a high protein content of 25… 37%, fats 1… 25%, carbohydrates 39… 50%, as well as vitamins and minerals. Also, priority direction of regulation of improve prescription structure , properties and ensuring stability of chemical composition of a thermostable filling is a tendency to implication of components of a plant origin: hydrocolloids, protein-oil and cereals [7; 9; 41; 91; 206; 209].

Significant contribution to the development of combined dairy and plant products goes to the scientific school of Kharkiv State University of Food Technology and Trade - Doctor of Technical Sciences, Professor, laureate of the State Prize of Ukraine, Academician of the International Cold Academy Pavlyuk R. Yu. - "Fundamental and applied research in the development and introduction into production of high technologies, including nanotechnology of the first domestic natural vitamin and antioxidant additives from various kinds of plant raw materials in the form of fine powders, homogeneous pastes, extracts and functional products with their use», as well as the scientific school of the Odessa National Academy of Food Technologies - Doctor of Technical Sciences, Professor Vinnikova L.G. and Doctor of Technical Sciences, Professor Bezusov A.T. - "Theory and Practice of Creating New Food Technologies". Also, a considerable contribution to the creation and expansion of the range of dairy products was made at the National University of Food Technologies, in particular, Doctor of Technical Sciences, Associate Professor Polishchuk G.E. - “Development of innovative food technologies of combined composition on the basis of activated plant raw materials” , as well as Candidate of Technical Sciences, Associate Professor Grek O.V. and others. The integrated use of dairy and plant raw materials has also been reflected in the meat industry. Staff of the North Caucasus State Technical University (Doctor of Technical Sciences, Professor Shipulin V.I., Candidate of Technical Sciences, Associate Professor Marchenko V.V., Candidate of Technical Sciences, Associate Professor Postnikov S.I. and Candidate of Technical Sciences, Associate Professor Statsenko O.M.) and the National University of Food Technologies (Doctor of Technical Sciences, Professor Pasichny V.M.and other scientists) have made significant achievement in the development of the meat industry in application of dairy and plant concentrates for improvement and creation of new types of meat products.

Under the guidance of these domestic scientists, new scientific data on the joint combination of dairy and plant components were obtained for creation new or improvement of the existing types of products with predefined physical, chemical, structural, mechanical, functional, technological and rheological properties. The obtained data formed the basis for the creation of a number of products, in particular therapeutic and prophylactic character, enriched with vitamins B, A, C, with the increased content of calcium, iodine, protein and dietary fiber. These products include advanced dairy drinks, yoghurts, cheeses sour-milk, kefirs, butter, sausage and other dairy and meat products.

It is worth emphasizing that cereals, beans, structure-forming agents have become widely used as plant raw materials. Protein-oil crops are less commonly used. However, due to the weighty direction of waste-free use of food raw materials, the relevance is acquired by protein-oil crops that enrich the product with plant protein and oil become, thereby contributing to a better balance of the chemical composition of the development. Protein-oil crops and products of their processing are widely used in bakery products, and much less - in the meat and dairy industries. The foreign scientists of the Siberian Research Institute of Cheesemaking of the Russian Agricultural Academy and the Kemerovo Technological Institute of the Food Industry make a great contribution to the development of this direction, in particular Candidate of Technical Sciences, Associate Professor Musynii O. and Candidate of Technical Sciences, Associate Professor Shulbaieva M. and domestic scientists of Kharkiv State University of Food Technology and Trade, Doctor of Technical Sciences, Professor Pavlyuk R. Yu., Doctor of Technical Sciences, Professor Pogarskaya V.V., Doctor of Technical Sciences, Professor Pertsevyi F.V. and National University of Food Technologies in the person of Doctor of Technical Sciences, Professor Rashevskaya T.O. and to other scientists who have worked in this field. On the basis of a number of new scientific data obtained, dairy products were developed with the involvement of protein-oil crops and products of their processing. [109; 217].

1.2 Substantiation of using thickeners and structure-forming agents in the technology of thermostable dairy-containing fillings

One of the main conditions for the effectiveness application of hydrocolloids is their complete dissolution, which depends on the chemical nature. Indicators of water solubility and features of the structure of some hydrocolloids are given in table. 1.2.

Features of structure formation depending on chemical nature are summarized in Table 1.3. The joint introduction of two different hydrocolloids given in table. 1.3, are accompanied by a synergistic effect, which can similarly be achieved by the ratio of individual thickeners with some biopolymers of protein nature [10; 12; 23; 83; 110; 124; 133; 165; 203; 232; 252; 255; 298]. Technological properties and perspective ways of their use in the food industry to provide the specified structural and mechanical properties are given in Table 1.4.

Table 1.2

Features of structure and solubility of hydrocolloids

Additive	Features of the structure	Solubility of hydrocolloid
Guar gum	Highly substituted polysaccharide	Soluble at room temperature
Locust bean gum	Areas in polysaccharide chains are not substituted	Soluble only when heated
Pectins	Branched and methoxy groups in polysaccharide chains; acidic, ionized groups; electrostatic repulsion between chains	Soluble at room temperature
Alginates	Electrostatic repulsion between chains	Soluble at room temperature
Carrageenans	3-, 2-, 1- sulfide groups on two galactose	Soluble when heated at room temperature
Xanthan gum	A large number of side chains in polysaccharide molecules; electrostatic repulsion due to the presence of acid groups	Soluble at room temperature

Table 1.3

Conditions of structure formation in polysaccharide solutions

Polysaccharide	Optimal pH range	Conditions of structure formation	Mechanism of structure formation
Pectin:			
– highly esterified	2,5–4,0	pH less than 4; Solids content = 55 – 80%	Sugar and acid
– low esterified	2,5–5,5	In the presence Ca^{2+}	Model of "egg packing"
Alginate	2,8–10,0	pH less or if present Ca^{2+}	Model of "egg packing"
Agar	2,5–10,0	At temperatures below 32…39° C	Model of double spirals

Table 1.4

Use of hydrocolloids in food industry

Technological function	Hydrocolloid	Field of application
Viscosity increase	Lambda-carrageenan, sodium alginate, xanthan gum, guar gum, locust bean gum, modified starches, modified cellulose	Sauces and various seasonings for salads, dairy desserts, soups, drinks, bakery products
Structure formation: - thermo-reversible gels	Kappa carrageenan, iota-carrageenan, low-esterified pectins,locust bean gum	Jams, thermostable fruit fillers, flavored milk gels, confectionery jams and confitures, pet food
- thermo-irreversible gels	Alginate of sodium, potassium or ammonium, high- and low-esterified pectins	Jams and confitures, pet food
Stabilization	Thickeners, low concentration of gels	Food emulsions, ice cream, fruit fillers, fermented milk products, chocolate milk

A lot of attention has recently been paid to confectionery products, which include hydrocolloids. The most common of the given above hydrocolloids are pectins and starch [10; 12; 23; 83; 124; 133; 158; 162; 190; 223; 262]. They are characterized by high functional and technological properties, low prime cost and simple technological use.

1.2.1 Substantiation of the expediency of using starch

A group of compounds – food hydrocolloids – the first time began to use in 1978 as a part of foodstuff to provide them with a predetermined consistency: viscous, plastic, or strong - and rheological properties [102; 104; 106]. Quite common hydrocolloids in the food industry that meet the modern requirements of manufacturers are agar, agarid, pectin, cellulose and its derivative starches, etc. [12; 21; 34; 45; 76; 126; 162; 187]. They are capable to perform the following functions: to protect the protein during thermal treatment, to stabilize the filler particles, preventing sedimentation, to improve the consistency of the finished product, to increase the viscosity of the system by binding of free moisture [23; 51; 56; 67; 102;

104; 220]. Depending on the final product, hydrocolloids are divided into two main groups: thickeners are substances used to give a product a viscous consistency; structure-forming agents - substances added to give a food product of a given consistency (jelly-like) [11; 54; 66; 211].

In the food industry, starch is often used as a thickener - native and modified for the preparation of kissels, puddings, sauces; it is also added to the dough (10%) during the production of biscuits, cakes and other products. It is used in the production of meat, pasta and sweets due to its ability to bind moisture, thereby preventing their sinerezis [48; 29; 126; 170; 254]. The main raw material for its production is potatoes, corn, wheat, rice, sorghum and others. Depending on the raw material starches have a number of features, namely: the size and a form of grain, viscosity and transparency of the formed paste, stability during storage, mixing and thermal influence [58; 120; 169; 213].

Starch is a natural polymer which contains in plants in the form of separate grains. It consists of amylose (10 - 20%) and amylopectin (80 - 90%), the monomer of which is α-glucose. It is little soluble in cold water, but in hot water swelling with the formation of starch paste. The degree of swelling of the starch depends on the temperature, the amount of water and the type of raw material from which it is made [107; 126; 168; 155; 187; 213]. During swelling in the middle of the starch grain creates voids where water gets in, breaks and weakens some of the hydrogen bonds between the chains, which causes the starch grains to expand. At the same time a part of polymers dissolves and remains inside the starch grain, and the part diffuses outward, forming a dispersion system. In the process of heating, the grain structure changes. Initially, during slow heating, there is limited swelling of the grains and the viscosity changes, but with increasing temperature, starch grains increase in volume several times, absorbing water, which leads to the formation of starch paste. This process is called starch gelatinization [23; 29; 43; 49; 50; 102; 169], its temperature is for potato starch 59…64 ºC, rye 50…55 ºC, rice 65…73 ºC, wheat 54…62 ºC, corn 80 ºC.

The main sign of formation of starch paste is system viscosity increase , which depends on the concentration of starch, surfactants, glycerides, speed of heating, temperature, mechanical influence, size of starch grains [29; 43; 49; 80; 87; 104; 168; 169; 174]. In the suspension forms a gel due to the aggregation to which amylose is capable, and the partial crystallization to which amylose and amylopectin molecules are capable, which is accompanied by the formation of hydrogen bonds between chains during cooling of the starch paste [118; 193; 170; 302]. During storage of starch gels, the phenomenon of syneresis and deterioration is observed due to retrogradation [29; 40; 210]. This process is characterized by the separation of bound moisture from the polysaccharide. It is displaced from the starch paste and the product becomes more rigid in consistency [83; 102; 118; 261; 300].

The use of native starch is quite wide. However, due to the inconvenience of its use and the difficulty of obtaining a product with the specified functional and technological properties, that is why the use of modified starches became popular [43; 50; 80; 86; 95; 118; 210; 254; 270]. It is worth noting that the major inconvenience of using native starches in food products, particularly during storage, is the ability of such starches to retrograde (aging), accompanied by syneresis. For elimination of this property, the starch is modified. For example, on OH-group of starch is acted by nitrogen, at the same time prevent the crosslinking of its molecules. Also, when starch is modified, the glycosidic bonds between the molecules are broken, accompanied by a decrease in viscosity, since the starch is crosslinked [43; 48; 86; 95; 103; 213 ; 277].

Due to the rather stringent technological conditions for the production of combined thermostable filling with the use of dairy raw materials and plant protein additives, its storage, especially in the frozen state, as well as during the implementation of the necessary technological qualities of development - thermal resistance under conditions of of high temperature influence - it is appropriate in technology of such filling to use modified starch with the necessary technological properties.

The specified properties are fully consistent with corn starch modified E1442 - oxypropylene dichromalphosphate crosslinked. It is the most popular among manufacturers. Such modified starch rapidly swells and forms a starch paste, is resistant to high temperature processing and cycles of freezing / defrosting while maintaining high viscosity characteristics [10; 29; 32; 43; 47; 49; 80; 83; 86; 103; 277].

1.2.2 Relevance of pectins engaging

One of the ways to improve the quality of confectionery products and provide heat-resistant properties of dairy fillings using dry skimmed milk is the use of hydrocolloids: pectin, alginate, agar, etc.

Hydrocolloids perform the following functions:

- provide protection of protein , allowing heat treatment;
- stabilize the filler system, preventing them from settling;
- improve the consistency of the finished product;
- bind free water, increasing the viscosity of the mixture [29].

Hydrocolloids are promising raw materials for improving organoleptic parameters, achieving the necessary viscosity, texture, structural and mechanical properties of products, thermal stability of milk fillings and fillers.

Food hydrocolloids are added to liquid or solid food products during their production in order to provide the required viscosity or consistency, as well as food dispersion systems (emulsions, suspensions) to stabilize them.

This group of compounds, which have the status of food additives, includes substances of two main functional classes: thickeners and gelling agents. Thickeners are substances that are used to increase the viscosity of the product. Gelling agents are substances that give the food product the properties of a gel (a structured highly dispersed system with a liquid dispersion medium that fills the framework formed by the particles of the dispersed phase).

Many food additives of this group have a related technological function of a stabilizer (compounds that form and preserve homogeneous dispersions of homogeneous substances), since increasing the viscosity of a dispersed food system when a thickener is introduced into it or turning such a system into a gel at low concentrations of a gelling agent prevents its separation into initial components, for example, precipitation of solid parts dispersed in a liquid dispersed phase [11].

If introduced into a liquid food system during the preparation of a food product, thickeners and gelling agents bind water, as a result of which the food colloidal system loses its mobility and the consistency of the food product changes.

The effect of changing the consistency (viscosity increase and gel formation) will be determined by the features of the chemical structure of the introduced additive.

Chemically, additives of this group are polar compounds (mostly polysaccharide in nature), in macromolecules that evenly distribute hydrophilic groups that interact with water, can also participate in exchange interaction with hydrogen ions, and especially calcium, and in addition, that with organic molecules of lower molecular weight: among them plant (pectin) origin, as well as substances that are obtained artificially - modified starches and others. One of the main conditions for the effectiveness of the use of hydrocolloids in the confectionery food system is their complete dissolution, which depends on the nature [12].

When water-soluble polysaccharides come into contact with water, solvent molecules first penetrate into the least organized parts of the macromolecular chain. Such an initial organization weakens the bonds in the latter and promotes the penetration of water and solvation of the most organized sections of the chain. This process goes through an intermediate stage of gel formation when the particles swell and increase in volume due to the cohesive forces between the macromolecules. If the intermolecular bonds are relatively weak, they can be broken quite easily by mechanical action or heating. At the same time, the biopolymer (polysaccharide or protein) is completely dissolved. But, if the connections between certain segments of macromolecules are not destroyed by mechanical or thermal action, the biopolymer is preserved in the form of swollen parts. Examples include alginate and calcium pectate.

Solubility increases in the presence of ionized groups (sulfate and carboxyl), which increase hydrophilicity (carrageenans, agaroids), as well as in the presence of side chains in polysaccharide molecules that branch the main chains, which improves hydration (xanthans). Solubility decreases in the presence of factors that contribute to the formation of bonds between polysaccharide chains: the presence of unbranched zones and areas without ionized groups (locust bean gum); the presence of calcium ions or other polyvalent cations, which cause cross-linking of polysaccharide chains, which prevents dissolution (pectin).

Depending on the chemical nature of the molecules and the characteristics of the food system, different ways of gel formation are possible.

In a number of cases, the joint intoduction of two different fillings of this group is accompanied by a synergistic effect. Similarly, the synergistic effect of increasing viscosity can be achieved by the ratio of individual thickeners with some biopolymers of a protein nature. These include, for example, combinations of carboxymethyl cellulose with casein or soy protein [13].

When choosing a hydrocolloid for the most effective solution to a specific technological problem, a number of aspects are guided by the following:

- • a specific task of regulating rheological properties (increasing viscosity or gel formation);
- • formation of the desired texture of the food product;
- • amount of filler to achieve the desired effect (formation of a given viscosity or a gel of a certain strength);
- • peculiarities of a certain food system (pH, chemical composition, etc.);
- • potential probability of interaction of the filler with the ingredients of the food system, i.e. competition with other water-soluble agents;
- • the temperature of the technological process and its duration at the specified temperature regime;
- • storage temperature of the finished product;
- • the possibility of effective dispersion on existing equipment;
- • economic feasibility, which is determined by the cost of the amount of filler required to obtain functional characteristics.

The use of hydrocolloids in modern food technologies makes it possible to create an assortment of structured and textured products of an emulsion and other food nature (margarines, combined oils, mayonnaise, sauces, marmalades, jams, candies, etc.).

Generalized examples of the use of the most well-known thickeners and gelling agents in food technology are given in table 1.5.

Table 1.5.

Application of gel agents and thickeners in the food industry

Technological function	Food supplement	Typical area of use
Increase in viscosity	Lambda-carrageenan, sodium alginate, xanthan gum, guar gum, locust bean gum, modified starches, modified celluloses	Sauces and various seasonings to salads, milk desserts, soups, drinks, bakery products
Gel formation: • thermoreversible gels	Kappa-carrageenan, iota-carrageenan, low-fatized pectins, locust bean gum	Jams, thermostable fruit fillers, flavored milk gels, confectionery
• thermally treated gels	Alginate of sodium , potassium or ammonium, high- and low-elateralized pectins	Jams
Stabilization	Thickeners, low gel concentrations	Food emulsions, ice cream, fruit fillers, dairy products, chocolate milk

Pectin is widely used in the confectionery, dairy, meat, baking and canning industries due to its high technological characteristics, which are manifested in the ability to bind moisture, acting as a thickener, structure-forming agent, system stabilizer [10; 19; 20; 63; 133; 266; 269; 276]. Besides, pectin and pectin-containing substances are able to influence positively a human body, namely [110; 120; 170; 190; 226 Hours; 265; 280]: bind ions of heavy metals, radioactive substances; to show immunomodulatory properties; to reveal therapeutic and prophylactic properties in case of disruption of the gastrointestinal tract, for people suffering from diabetes and other diseases [6; 51; 63; 79; 87; 110; 117; 120; 157; 170; 216].

Pectin is characterized as a natural structure-forming substance which is contained in the cellular walls and intercellular space of all plants, and determines the regulation of water metabolism and the fulfillment of various physiological functions, both structural and binding components in plant tissues [10; 23; 76; 66; 83; 173; 247; 248; 265; 271; 290].

The most common raw materials for pectin production are citrus and apple pomace, sugar beet cake and sunflower core [21; 55; 68]. For the most part, pectin is contained in the peel, lamellae and cores of fruits and berries (table 1.6).

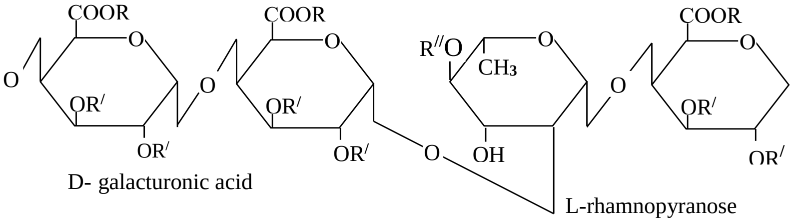
Table 1.6

Concentration of pectic substances in fruits and vegetables

Fruits and vegetables	Concentration of pectic substances, %
Apricot	0,4–1,3
Quince	0,5–1,1
Cherry plum	0,6–1,1
Orange	0,6–0,9
Cherry	0,2–0,8
Wild strawberry	0,5–1,4
Cranberry	0,5–1,3
Gooseberry	0,2–1,4
Lemon	0,7–1,1
Raspberry	0,2–0,7
Tangerine	0,3–1,1
Peach	0,6–1,2
Plum	0,8–1,5
Black currant	0,6–2,7
Red currant	0,4–0,7
Sweet cherry	0,6–1,6
Apple	0,8–1,8
Carrot	1,0–1,4

There are two main types of pectic substances in plants: protopectin is characterized by a complex structure of the molecule, is insoluble in water, alcohol and ether; pectin, or soluble pectin, consists of water-soluble polygalacturonic acids, which are formed from protopectin by the action of acid, alkali or the enzyme of protopectinase [55; 158].

Pectic substances are plant polysaccharides, which by their chemical structure (Fig. 1.1) are macromolecular compounds which are the basis of a chain of 1-4 glycosidic bonds, residues of D-galacturonic acid and a certain amount of residues of 2-O-substituted L-rhamnopyranose that joins to the main chain. In the form of side chains in a small amount there are residues of neutral monosaccharides of L-arabinose, D-galactose, D-xylose, fructose, etc., this indicates that pectic substances are heteropolysaccharides [33; 46; 87; 173; 183; 190; 248; 264; 287; 289]. Much of the galacturonic acid residues are bonded to the metal groups.



R = H or CH_3;
$R^{/}$ = H, CH_3CO, less often a carbohydrate chain;
$R^{//}$ = H or a carbohydrate chain

Fig. 1.1. Chemical structure of pectic substances

At the time when human life occurs in the conditions of severe environmental aggression, this is not enough. Such components are needed in nutrition, which would contribute to the prevention of chronic intoxication, the elimination of pesticides and heavy metals of radionuclides from the body, that are interrupted in it.. Over time, high detoxification properties of pectin were confirmed in different countries and in our country with its absolute harmlessness [3,9].

By chemical and enzymatic treatment, it becomes one of the most jelly ingredients. The source of raw materials, as in the classic scheme, are citrus, beet and crop production waste.

Apple pectin extract is produced in three types: A, Б, B, which differ in the mass fraction of pectin substances: in A - 0.4...1.0%, Б - 1.1...1.5%, B -1.6...3 .0% [10].

Along with pectin substances, pectin extract contains such biologically active substances as proteins, digestible sugars (glucose, fructose), organic acids, complexes of macro- and microelements. The extract has good organoleptic properties: a pleasant apple aroma, sour taste, allows you to use it as a drink.

The presence of free carboxyl groups of galacturonic acid in pectin substances determines their ability to bind metal ions (lead, mercury, cobalt, cadmium, zinc, chromium, nickel and their compounds) in the gastrointestinal tract, as well as radioactive strontium, cesium, zirconium and others with subsequent formation of insoluble complexes (pectinates, pectates) that are not absorbed or excreted from the body [14].

An important condition that determines the properties of pectin, its solubility and structure formation, is the degree of esterification, characterized by the ratio of esterified groups of galacturonic acid to its total amount [53; 259; 264]. Depending on the degree of esterification pectin is divided into: highly esterified (more than 50%); low-esterified (less than 50%).

Highly esterified pectin is traditionally used in the confectionery industry: in the production of marmalade, jelly candies, marshmallows and pastels, jams and jam for flour products. The use of such pectins requires compliance with strict technological parameters, in particular, a high temperature of formation and precise pH values in a narrow range. At the same time, pectin jelly should be used immediately after adding solutions of citric or lactic acid, as it is irreversible. Highly esterified pectins form jelly in the presence of three more ingredients: water, sugar and acid, the role of each of which can be represented as follows: pectin, soluble in water, partially dissociates, forming COO- ions, as a result of which the molecules acquire a negative charge and a force arises between them repulsion [3].

The first rule to follow when working with highly esterified pectins is that gelatinization occurs only when the soluble solids (mainly sugar) are between 60 and 80%. The solubility of sugar (sucrose) in water is limited and and makes up 67% (at normal temperatures). For this reason, in the production of jelly with a high content of soluble solids, it is necessary to additionally use other, more soluble sugars.

The presence of sugar leads to a decrease in the solubility of pectin in water, and the addition of acid suppresses the ionization of pectin, which makes it possible to counteract the electrostatic repulsion of molecules, and as a result, transition zones are formed.

In the case when fruits are not included in the recipe, when working with confectionery fillings, it is most often useful to add acid at the final stage of cooking and include invert sugar or liquid glucose (corn molasses) as one of the main ingredients. This allows for more accurate regulation of the proportion of invert sugar in the finished product [4].

The presence of liquid sugar and/or liquid glucose prevents the crystallization of sucrose in the filling, if the concentration is from 67 to 80% of soluble solids. During the production of fillings, it is necessary to ensure the minimum level of soluble solids content - 75% concentration, therefore the zone of optimal jelly formation decreases.

In order to make a good jelly, it is especially important to consider the acidity of the mixture, which should be considered as pH (active/true acidity) as the presence of buffer salts can reduce the acidity. For highly esterified pectin, the pH range that ensures optimal jelly formation is 2.9...3.6, since at a pH above 3.6 jelly formation occurs only partially and pectin is wasted. Pectin jelly can be considered as a system in which the polymer is in a state between fully dissolved and precipitated. In theory, the mechanism of pectin gelation is as follows: segments of the molecular chain connect to each other as a result of crystallization and form a three-dimensional network that holds water, sugar and other solvents

The formation of jelly, from the state of a completely soluble polymer, is caused by physical and chemical changes that reduce the solubility of pectin, which contributes to the formation of local crystallization. The most important factors of pectin dissolution are: temperature, composition of pectin molecule (type of pectin), pH value, sugar and other solvents, calcium ions.

The gelation mechanism of highly esterified pectin occurs according to the scheme:

- methoxyl groups as a hydrophobic part of pectin prevents contact with water - pectin chains gather together, gelation is possible;
- dissociated carboxyl groups - repulsion of pectin chains, negative effect on gelation;
- non-dissociated carboxyl groups - positive effect on gelation;

- sodium bonds of carboxyl groups, repulsion of pectin chains, further, a large hydrate shell - negative effect on gelation;
- potassium bonds of carboxyl groups, a smaller hydrate shell - the calling effect of gelling;
- hydrogen bonds between pectin chains and hydroxyl groups - gelation.

Low-esterified pectins of various brands are more flexible and interesting in terms of technological possibilities, which significantly expand the area of use of confectionery masses based on pectins and open up new perspectives for manufacturers. Due to their ability to jelly formation under various conditions, low-esterified pectins are increasingly used in the food industry, as well as in the production of cosmetics and pharmaceutical products [16].

The most important difference between low-esterified pectin and high-esterified pectin, which determines the conditions of its jelly formation, is the degree of esterification. The boundary between highly esterified and low-esterified pectins is the degree of esterification of 50%. It determines the properties of pectin, in particular its solubility and gelatinization characteristics. If the content of sugar or soluble solids is high (as, for example, in confectionery jellies), the jelly formation temperature increases.

Low-esterified pectins are obtained from high-esterified pectins by de-esterification of the latter with acid or alkali under controlled conditions.

High-esterified and low-esterified pectins have different gelation mechanisms. Jelly formation of highly esterified pectins occurs in systems containing at least 55% of dry matter in the presence of acid, while the pH should be 2.8 - 3.5. In contrast to highly esterified pectin, sugar and acid are not particularly important for jelly formation, since when using low-esterified pectin, the mesh structure of the jelly is formed due to calcium pectinate. It is possible to prepare jelly, in which the content of dry substances will be only 2%, and the pH is close to neutral, but this does not mean that you cannot make a filling with the addition of sugar - sometimes acid can be added for taste and to increase the shelf life of the product (provided that , that calcium salts are present) [35].

A mandatory condition for the gelation of low-esterified pectins is the presence of calcium ions or other divalent cations in the system. Jelly formation on low-esterified pectins is possible at any, even low enough dry matter content. At the same time, low-esterified pectins are characterized by a decrease in the gelation temperature with a decrease in the content of dry substances in the system. The degree of esterification of low-esterified pectins determines their chemical activity with calcium. The lower the degree of esterification of pectin, the brighter its resemblance to polygalacturonic acid and the higher the activity with calcium, which is expressed in higher gelling temperatures. Low-esterified pectin with a degree of esterification of 35% practically does not form of jelly without calcium. The presence of amide groups in low-esterified pectins reduces its hydrophilicity and increases the ability to form jelly. Amidated low-esterified pectins have a wide range of activity with calcium. At the same time, with an increase in the degree of amidation, they form jelly at higher temperatures.

The gelling process of low-esterified pectins is a reaction that is more dependent on temperature. To fully characterize the process, it is necessary to accurately determine the temperature at which gel formation occurs after cooking. At this temperature, which is also called the gelation temperature, the transition of the liquid prescription mass into the jelly state occurs. At this stage, the orientation of pectin molecules and the formation of a three-dimensional spatial structure in which water and sugar are in a bound state occurs. Mechanical action, for example, pumping and (or) stirring at a decrease in temperature interfere with the spatial orientation of molecules and destroy the associations of pectin chains that have already formed. In this case, it is impossible to form a strong and homogeneous jelly structure. After the end of the mechanical action at temperatures significantly lower than the gelation temperature, a new reorientation of pectin molecules, and therefore the formation of a strong gel, is practically impossible. This requires reheating the entire system to a temperature above the gelation temperature. The gelation temperature of jelly based on low-esterified pectins depends on the dosage of calcium. Increased dosage of calcium leads to intense convergence of pectin molecules even at high temperatures (above 80°C). Thus, if all other parameters of the product are maintained at a constant level, the gelation temperature increases with a simultaneous increase in calcium dosage [41].

The mechanical action during gelation always occurs when the jelly is poured. If pouring occurs at the temperature of the pasty structure due to the effect of premature gelation. In this regard, knowledge and the whole directed use of such concepts as "gelling temperature", "pouring temperature" and "premature gelation" form the basis for the successful use of low-esterified pectins in the production of heat-resistant fillings. A change in the level of the above-mentioned parameters leads to a purposeful change in the strength, consistency, heat resistance and surface gloss of the filling.

- Low-methoxylated pectins also include amidated low-methoxylated pectins. Such pectins have advantages compared to ordinary low-methoxylated pectins:
- • the jelly obtained is thermoreversible, that is, it melts when heated and solidifies again when cooled;
- • amidopectins have thixotropic properties - at a temperature slightly below the gelation temperature, their fluidity can be maintained by stirring, and jelly formation occurs immediately after its termination;
- • syneresis is significantly reduced.
- • the content of soluble solids is not limited.

The gelation process of low-esterified pectin is also affected by the type of sugar or sweeteners, just like high-esterified pectin. Thus, the need for optimal gelation when forming a jelly based on sorbitol is greater than when using sucrose. The same effect is observed in the case of using fructose. Each type of LEP is characterized by different sensitivity to calcium ions. During the process of gradual de-esterification, the number of carbon groups in pectin particles increases, accordingly the need for the presence of calcium ions increases.

No less significant influence on the dosage of calcium salts is provided by the type and concentration of buffer salts. An increase in the concentration of buffer salts, especially those capable of binding calcium, leads to an increase in the content of calcium ions introduced. Such buffer salts include, in particular, salts of citric acid.

The dosage of calcium should be increased with an increase in the pH value, a change in the pouring temperature of the mass of the desired structure. Thus, with its increase, a greater number of calcium ions can be incorporated into a given structure without premature gelation.

Thus, the change in calcium dosage can be controlled not only by the strength of the structure, but also by its rheological and organoleptic indicators. With a very low concentration of calcium, jelly products are characterized by high viscosity or a slightly gelatinous texture, with an average - the necessary structure is formed that "spreads on the tongue". At a high concentration of calcium salts, an elastic structure is formed, but its ability to syneresis increases.

A factor affecting the temperature and rate of gelation is the presence of some buffer salts, since the addition of these salts prevents premature gelation. For this purpose, the sodium salt of citric acid and various sodium polyphosphates are more often used.

The use of highly esterified pectin requires strict technological conditions: high temperature of formation and clear pH values. In this case, for formation of the gel it is necessary to adhere to certain conditions: the solids content of at least 55%, the pH value in the range of 2.8 ... 3.5, which is achieved by the addition of lactic or citric acid [34; 133; 232; 259].

Instead, the conditions for using low-esterified pectin are much simpler. It is known that low-esterified pectin requires the presence of divalent metal ions (Ca^{2+}) in the system, but the realization of the functional and technological properties of such pectin does not depend on the pH value and the amount of solid [77; 128; 195; 220; 283]. First of all, the process of gel formation of low-esterified pectin is influenced by the gelation temperature and the amount of divalent metals in the system, namely: for insignificant their content rapprochement and orientation of molecules of pectin occurs, with increasing gel is formed, and in case of overdose it precipitates, forming calcium pectinate with premature gelation [153]. Gels of high- and low-esterified pectins should be formed by reducing the polarity of the water and increasing the surface tension and viscosity by adding sugar. The formed dispersion system promotes the aggregation of hydrophilic pectin molecules, which partially dissociates into COO- ions, owing to what they get a negative charge. When the pectin molecules converge to the distance of overlap of their diffusion layers, repulsive force arises between them. Its neutralization requires the introduction of an indifferent electrolyte (organic acid or divalent metal ions) into the system. In this case, the force of electrolytic repulsion is weakened and becomes equal to zero [29; 36; 111]. The mechanism of gels formation of high- and low-esterified pectin is to connect segments of spiral molecular chains due to crystallization, which leads to the formation of a three-dimensional network that holds water, sugar and other solvents. For the normal course of the gelation process, the molecular weight of the pectin should be at least 20 000 [83; 210].

1.2.3 Modern theories of pectin gelation

Modern theories of pectin gelation assume the presence of characteristic zones in pectin molecules, created from disordered connected pectin chains. Together with these zones, there are also fragments of free unconnected chains, which are the result of the presence of acetyl groups, rhamnose and side chains. Such a structure has the character of a grid and at the same time prevents the formation of insoluble chains. In the process of gelation, filamentous pectin molecules in the presence of various additives (sugar, acid, calcium ions) form a three-dimensional framework.

The most widely accepted theory of pectin gel formation is based on the following assumptions:

- pectin is a hydrophilic colloid;
- sugar is considered as a dehydrating factor;
- the introduction of food acids contributes to a significant reduction of the negative charge of the pectin macromolecule, which creates conditions for the relative convergence of molecules and the emergence of hydrogen bonds between them;
- the process of dehydration of pectin macromolecules and the formation of hydrogen bonds between them takes place over a period of time, just like the processes in other polymer systems;

- the rate of pectin dehydration increases as the concentration of hydrogen ions increases;
- the maximum strength of the gel is noted at ionic equilibrium.

Gel formation depends on the molecular weight of pectin, the esterification of its molecule and the content of functional groups, the concentration of sugar in the solution, the amount of ballast substances accompanying this pectin, the temperature and pH of the medium. Taking into account the degree of esterification of pectin molecules, two types of gels are distinguished: with side and main valence .

Acid-sugar pectin gel are formed due to hydrogen bonds with the participation of non-dissociated free carboxyl groups. This type of gel is typical for highly esterified pectins. Low-esterified pectins form gels only in the presence of Ca^{2+} ions. At the same time, pectin molecules interact with each other due to free carboxyl groups, which are bound by Ca ions into a strong framework. Such gels are called ion-bound. In addition to these main ones, the formation of intermediate gels containing both sugar and Ca-ion is possible. Such gels are typical for pectins with a degree of esterification of about 50%, in particular, for beet pectin.

Depending on the conditions under which the gel is formed, its structure is created with unequal quantitative participation of various bonds. The acid added for gelation displaces cations from the pectin molecule, creates free carboxyl groups, reduces their dissociation, neutralizing electrostatic forces of repulsion between pectic acid molecules. The strongest jellies are formed in the presence of citric, tartaric and trioxyglutaric acids.

Sugar acts as a dehydrating agent during gelation. The highest gel strength is achieved when sucrose is added, the lowest – maltose. For the formation of a strong gel in the three-component pectin-sugar-acid system, their optimal ratio is necessary, which is not absolute, but depends on the type of pectin, which determines the limits of the ratio of the components of the recipe mixture. In practice, the optimal condition is an approximate ratio of pectin:sugar:acid - 1:60:1.

It should be noted that, despite the fact that the optimal pH value for obtaining gels of maximum strength is often indicated in the literature, there is no scientific explanation of the relationship between pH and pectin's ability to gel. The chemical structure of the pectin macromolecule has a significant effect on jelly formation. Pectic acid, in which all residues of galacturonic acid have carboxyl groups, is insoluble in water and does not have the ability to gel. The presence of ballast substances bound to pectin by valence bonds (for example, with other polysaccharides) causes a change in the conformation of its macromolecule and negatively affects the formation of the gel and its strength. Acetyl groups bound to hydroxyl groups of pectin substances significantly impair their ability to gel formation. The largest amount of acetyl groups is contained in pectin from sugar beet (0.38...0.80%), from sunflower baskets (0.45...0.90%), causing their low ability to gel.

We studied the possibility of increasing the properties of sugar beet pectins to gel formation by treating them with chemical reagents. Thus, the use of ammonium persulfate or hydrogen peroxide leads to an increase in the molecular weight of soluble pectins due to cross-linking and is accompanied by the formation of a strong gel. The gelatin obtained in this way has a high water-holding capacity and can be widely used in the food industry.

For highly esterified pectins, gel formation is due to two main factors: 1 – the addition of sucrose or other sugars leads to the dehydration of pectin molecules, which facilitates the convergence of polymer chains with each other and makes possible the formation of a silt structure through hydrogen bonds; 2 – lowering the pH of the medium suppresses the dissociation of free carboxyl groups and thus reduces the electrostatic repulsion between the chains. The described mechanism has so far been briefly referred to in the literature as "sugar-acid gelation".

However, recent research results confirm that pectins with a high degree of esterification are stabilized in a gel by a combination of hydrophobic interaction and hydrogen bonds, and therefore the concept of "sugar-acid gelation" must be explained in more detail. Methyl ether groups are hydrophobic parts of the pectin molecule. Under the influence of hydrophobic forces, they are grouped into aggregates, and they try to have the smallest possible contact surface with water. In addition, hydrogen bonds, for example, between non-esterified carboxyl groups are formed when the pH value of the gel is sufficiently low and the dissociation of carboxyl groups is largely suppressed.

In general, hydrogen bonds stabilize the pectin network, but without hydrophobic interactions of methoxyl groups, gelation would not occur for energetic reasons. The higher the degree of esterification, the greater the contribution of hydrophobic forces to gelation. The share of hydrogen bonds that are formed through free non-esterified groups decreases, and at too high a pH value, the influence of negative factors (-COO-) decreases, at a very high pH value of the product, dissociated carboxyl groups interfere with the formation of a spatial structure. This affects the pH range of gelation. Suppression of dissociation at very high values of the degree of esterification will not be so significant. The higher the degree of esterification, the greater the pH at which gelation begins. Fully esterified pectins do not need acid to form a gel. The necessity of a high concentration of sugar for the gelation of pectins with a high degree of esterification is explained by the fact that certain sugars stabilize the hydrophobic interaction. The addition of sucrose leads to the dehydration of pectin molecules in the solution and allows the pectin chains to approach each other, so that cross-linking of molecules through hydrogen bridges becomes possible. A decrease in pH prevents the dissociation of free carboxyl groups, which in turn reduces the repulsion of negatively charged pectin chains.

Gel formation by highly esterified amidated pectins takes place with the participation of sugar and acids (sugar-acid mechanism), and is not much different from the mechanism of gel formation by highly esterified non-amidated pectins. The presence of amidated groups in the pectin molecule in a hydrated state leads to certain spatial changes at the beginning of the reaction, which leads to a slower formation of associates between amidated pectin molecules than during the gelation of pectins with a high degree of esterification. In the final stage of the reaction, amidated groups additionally stabilize the gel structure, forming hydrogen bridges, which leads to the formation of a strong gel with an elastic-viscous structure.

The mechanism of gel formation of low-esterified pectin is significantly different from the mechanism of highly-esterified pectin. For gelation to occur in a system containing low-esterified pectin, the presence of calcium ions must be a decisive factor. These pectins form gels at a much lower solids content than highly esterified pectins, and also allow greater pH fluctuations that do not affect gelation. Unlike highly esterified pectin, jelly based on low-esterified pectin melts when heated. It is obvious that the gelation conditions of low-esterified pectin substances are not at all suitable for highly-esterified pectins, but there are general features in the behavior of macromolecules and their properties. Low-esterified pectins, like high-esterified ones, form interchain supramolecular structures only due to carboxyl groups, which are connected to each other by "calcium bridges".

The mechanism for the gelation of low-esterified pectin is associated with a well-known structure called the "egg box". The intermolecular interaction takes place by the side-to-side mechanism of interacting galacturans with the formation of parallel bonds of adjacent chains, which are bound by intramolecular electrostatic forces and ionic bonds through carboxyl groups. The strength of bond formation depends on the strength of electrostatic interactions. These bonds are strong if seven consecutive carboxyl groups are involved in the interaction. The presence of esterified groups in the interaction zone limits the formation of gels. All low-esterified pectins form supramolecular structures according to a single principle.

Another important condition for the gelation of low-esterified pectin is a high molecular weight. The strength of the gel is determined by the number of effective intrachain interactions. The lower the molecular weight, the shorter the chain and the less strong the gel. The effect of Ca^{2+} ions on pectin's ability to gel is practically imperceptible if 40% or more of the carboxyl groups are esterified. Calcium residues are especially effective in those parts of the molecules where 7 of the 15 carboxyl groups, located in sequence, are non-esterified. The presence of rhamnose-type monosaccharides in the primary structure of pectin, the spatial position of which is incompatible with the geometry of the crosslinking zones of galacturonic acid, negatively affects of gel formation. In citrus and apple pectin, the residues of these sugars are generally included in the side chains. These chains complicate the spatial orientation of molecules, necessary for the formation of interaction zones.

The interaction of pectin with calcium ions is complicated by the presence of acetylated fragments in the molecules, as their size is incompatible with the spatial arrangement of the chain with the chain within the interaction zones. Therefore, the presence of acetyl groups reduces the gelation ability of low-esterified pectins. This is especially characteristic of the gelation of beet pectin, in which the content of acetyl groups reaches 35 mol per 100 mol of pectin. Amidation increases the gelation ability of low-esterified pectin. Amidated pectins are less demanding on the presence of Ca^{2+} ions and do not form a precipitate at a high concentration of calcium ions compared to other pectins. Amidated pectins fit well into the "egg box" gelation system due to the formation of a system of hydrogen bonds in the product.

In addition, there are a number of other factors that affect the gelation of low-esterified pectin. These include the ratio of concentrations of pectin and Ca^{2+} ions, pH, ionic strength, dry matter content, and temperature. The gel formation of L-pectin without sugar is slightly dependent on pH. To increase the ability to gelation at low pH values (from 3.5), it is necessary to add more Ca^{2+} to pectin than at neutral pH values. The transition of the sol into a gel is faster with a decrease in pH due to a decrease in the number of dissociated carboxyl groups. At low pH values, the negative charge of the pectin macroion is neutralized by hydrogen ions, which leads to the formation of a precipitate. An increase in the ionic strength of the solution leads to a general decrease in the content of ions necessary for gel formation. Given the precipitation parameters, the gel of low-esterified pectin containing NaCl will have greater strength than the gel without salt. This effect is explained by the fact that when the concentration of NaCl increases, the charge of the macromolecule increases significantly, contributing to the increase of pectin molecules, and in turn leads to a decrease in the length of ionic bonds between polymers. At the same time, the rate of galation decreases and the number of crosslinking zones increases, which contributes to the stabilization of the gel in general.

Homogeneous gels of low-esterified pectins are thermally reversible. The structure of such gels is thermoplastic. An increase in temperature affects intermolecular bonds. Usually, the dispersion of such pectin in an aqueous solution takes place at elevated temperatures. It was established that the energy of intermolecular interactions is about 70 kJ/mol^{-1}. This value is four times higher than for highly esterified pectin. The temperature of the sol-to-gel transition increases with an increase in the content of pectin and calcium ions and a decrease in the degree of esterification.

Amidated low-esterified pectins normally form gels in jams, preserves, fillings, marmalade even with the amount of Ca^{2+} ions contained in fruit and water. Non-amidated low-esterified pectins usually require an increased calcium content to ensure gelation. The degree of esterification and amidation determines the reaction to Ca^{2+} of this or that low-esterified pectin. In practice, the degree of esterification and amidation together determine the relative gelation temperature of these pectins. Accordingly, low-esterified pectins can be classified as "fast" and "slow" or those, wich more or less responsive to Ca^{2+} . The combined effect of reducing pH and adding sugar promotes gel formation at a low content of Ca^{2+} ions. Despite the decrease in the number of ionized carboxyl groups, gel formation is enhanced due to the specific effect of sugar on water activity and hydrophobic interaction in the system. The strength of the gel also depends on the type of sugars. Low-esterified pectins are used in the production of low-calorie jellies with the addition of no more than 30-40% sugar.

Ca^{2+} ions or other multivalent cations are required for the gelation of amidated low-esterified pectins, as well as non-amidated pectins. But amidated pectins have a larger calcium dosing interval, that is, they form strong gels with a small amount of Ca^{2+} ions. Sometimes the calcium concentration in the fruit is sufficient. However, a high concentration of Ca^{2+} is necessary in order for premature gelation to be clearly manifested. Another difference between amidated and non-amidated pectins with a low degree of esterification is the dependence of the gelation temperature on the Ca^{2+} concentration.

Characteristic for pectin are reactions with di- and polyfunctional compounds that can cross-link pectin molecules into three-dimensional mesh structures through linear sections, forming water-soluble, stable, thermo-irreversible gels bound by main valences. Pectin substances can form derivatives obtained by the interaction of secondary hydroxyl and carboxyl groups. Cross-linking of pectins with formaldehyde (in the presence of hydrochloric acid as a catalyst) occurs quite easily due to the trans-placement of hydroxyl groups at the second and third carbon atoms. Crosslinking between two carboxyl groups of pectin chains is possible upon interaction with erythrodioxide or mustard gas. Cross-linking causes the formation of modified forms of pectin and changes in its structural and mechanical properties. A feature of beet pectin gel formation is crosslinking with the help of peroxidase enzyme and hydrogen peroxide according to the reaction, the feature of which is the interaction of ferulic acid residues located in branched fragments.

Comparing the gels of highly and low-esterified pectins, it should be noted that the weak-looking gels of HEP are characterized by rather high values of the modulus of springiness, elasticity and strength, while the "strong-looking" gels of low-esterified pectins differ in very low rheological indicators. Pectin and pectic acids form a gel in the presence of Ca2+ or other divalent cations. This effect is due to the formation of calcium bridges between correspondingly located carboxyl groups, although, according to Rees, the energy of such simple electrostatic attractions is probably too small to be considered an important factor in gelation. Both the placement of carboxyl groups in the macromolecule and the presence of other substituents significantly affect gel formation. Therefore, pectins from beets and potatoes, containing a large number of O-acetyl residues, are not a complete raw material for obtaining industrial pectin as a gelling agent. The ability of pectin to gel formation is also affected by the placement of methoxyl groups in pectin chains. If the chains have large fragments without methoxyl groups alternating with zones with esterified carboxyl groups, then such pectins have a lower ability to gel formation, which corresponds to their degree of esterification.

1.2.4 Mechanism of structure formation and gel properties of low-esterified pectin

In confectionery thanks to simple technological application conditions began to use low-esterified pectin. The results of the market analysis indicate that the considerable share is made by citrus low-esterified pectin. As mentioned above, it is able to form a gel in the presence of divalent metals, preferably calcium ions, regardless of the solids content and pH values [111]. The process of gelation of low-esterified pectin is shown in Fig. 1.2.

In case of introduction of ions of calcium, the polymer chains begin to be grouped and bind at the expense of polyvalent cations (Ca^{2+}), forming calcium bridges. During rapprochement of pectinaceous molecules which have zigzag-like form, cavities are formed that contain carboxyl and hydroxyl groups. They promote the association of pectin chains through the interaction and formation of complexes with calcium. The concentration of calcium ions plays an important role in revealing the properties of the gel: if their quantity is insufficient, the gel is not formed, and at excess, a gel is prone to syneresis and precipitation in the form of calcium pectinate salt, ie premature gelation occurs [47; 232 ; 275 ; 285].

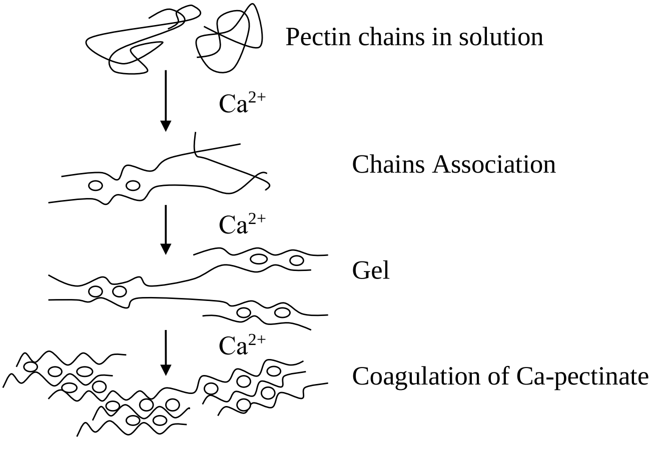


Fig. 1.2. The mechanism of gel formation of low-esterified pectin

The number of entering of calcium into a system is affected by the solids content, the type of sugar substitute and the buffer salt. At content about 60% it is not necessary to bring calcium ions, and at 20-30% it is necessary to add a significant amount, since no gelation will occur. It should be noted that the less solids in a product, the more calcium ions required. The formation of a gel of low-esterified pectin is to some extent influenced by the type of sugar or sugar substitute. Gel formation based on sugar substitute requires more calcium for optimum gel formation than when sugar is used. On the dosage of calcium salts have no less influence the dosage and concentration of the buffer salt. Increasing its concentration, especially of the salt that is able to bind calcium, leads to increase in a dose of entering of calcium into a system. Such is preferably citric acid salt [47; 81; 111; 184; 286]. If the concentration of calcium ions is exceeded in the pectin solution, a brittle gel is formed with a tendency to syneresis and lumps are sometimes formed, indicating that calcium precipitates, that is, the occurrence of calcium pectinate. Thus, changing the amount of calcium input it is possible to influence not only the strength of the gel, but also its rheological and organoleptic properties.

In modern technology practical use was found by salts of calcium chloride and calcium citrate. Calcium chloride salt is characterized by a fairly strong ionic strength [127]. According to the normative document (Order No. 222 of 23.07.1996), it is used in a limited amount, since the excess quantity degrades the organoleptic properties of the pectin gel: it acquires a bitter taste. An unlimited amount of calcium citrate salt can be used. Although this salt has a lower reactivity, it contributes to the formation of a plastic, uniform consistency of the pectin gel. Also, on the properties of pectin gel the great influence is rendered by the recipe components that are added to the composition of the food product.

1.2.5 Technologies of pectin products from plant raw materials: apple pectin concentrate, liquid pectin, dry pectin extracts, pectin-containing puree

The domestic food industry is focused on the use of pectin as a gelling agent in the production of jelly confectionery and canned goods for mass consumption, for which highly esterified apple and citrus pectin is traditionally used. Pectin is widely used in the production of products for preventive and health purposes, such as beverages, dairy, bakery, etc., consumed daily, and in which pectin is used as a structuring agent, detoxifier, complexing agent, that is, there are no high requirements for gelling ability [1, 3, 4, 5, 6, 7].

In the production of pectin foods there is the dissolution of dry pectin in water, juices, which is a labor-intensive operation, because pectin has a high hygroscopicity, forms lumps on contact with water [2]. The stage of pectin dissolution can be eliminated, and the costs of pectin producers and consumers can be significantly reduced due to the production of pectin extracts from various raw materials. Similar to liquid fruit and vegetable extracts due to manufacturability - the possibility of using hydraulic vehicles, storage in containers, ease of dosing, etc., pectin extracts are widely used in the food industry [43, 44, 59].

The application of hydrolytic nutrients (electroactivated water, citric, lactic, orthophosphoric acid, etc.) makes it possible to use pectin extracts as independent products for prophylactic purposes, as well as food additives in the production of consumer goods. Therefore, the composition of pectin extracts is subject to the following requirements:

- pectin extracts must not contain substances of toxic, carcinogenic, mutagenic or other harmful effects on the human body;
- according to the numerical values of safety criteria, the extracts must meet the indicators for beverages, and must not exceed the permissible levels of toxic elements, microbiological contamination;
- pectin extracts must contain such quantity of pectin and such quality that would allow them to be used as a food and biologically active additive [57].

Classification of pectin extracts

Depending on the type of raw material, pectin content and purpose, pectin extracts are divided into:

- by type of raw material: apple; citrus; fruit and berry; beet; carrot.

- by pectin content: extract type A (pectin content 0.5 ... 1.0%); extract type B (pectin content 1.1 ... 2.0%); concentrate (pectin content 2.0 ... 4.0%); dry extract (pectin content 10 ... 40%).

- by purpose: food additive (as a structurant of food technological environments in the production of bakery, dairy, confectionery, canned goods, etc.); dietary supplement (as a radioprotectant and detoxifier, for preventive and health products); when creating dosage forms and pharmaceuticals; for the production of cosmetics and detergents.

Extractive substances of pectin-containing raw materials

When extracting pectin substances from plant raw materials, other water-soluble substances are extracted from it: carbohydrates, proteins, starch, organic acids, polyphenols, dyes, macro- and microelements, which are ballast relative to pectin, but increase the biological value of pectin products [16].

The main part of plant cell juice is carbohydrates (glucose, fructose, sucrose and other oligosaccharides).

Up to 30% of cell juice remains in the raw material after pressing. In addition, in the process of hydrolysis of protopectin there is the destruction of molecules of starch, hemicelluloses, cellulose, resulting in the formation of soluble carbohydrates, the composition and amount of which depend on the type of plant. For example, fresh apple pomace contains 6.0 ... 8.0%, in the process of hydrolysis their number increases to 6.7 ... 8.3%. Pre-washing of apple pomace before hydrolysis reduces the dry matter content in the raw material to 2.0%, carbohydrates to 0.7% [20].

Depending on the type of plants, they are dominated by certain carbohydrates: glucose is contained in significant quantities in grapes, plums, raspberries; fructose - in grapes, apples, pears, black currants; sucrose - in sugar beets, apricots, citrus fruits, carrots. This causes a variety of mono - and disaccharides of pectin extracts.

The amount of protein in fruit and vegetable crops is insignificant (in currants - 1.0%, plums - 0.2%; rowan - 1.4%, apricots - 0.9%) and most of them are enzyme and membrane systems. In the process of acid-thermal treatment of raw materials is the denaturation of proteins, the permeability of plant tissue increases and some proteins are extracted from raw materials [9, 11, 12, 14].

Starch is contained in pectin-containing raw materials in small quantities and a significant part of it is hydrolyzed during heat treatment. In pectin extracts - 0.1 ... 0.5% starch.

Together with pectin-containing substances, polyphenols are extracted from plant raw materials: anthocyanins, leukoanthocyanidins, catechins. Their content in plant raw materials depends on the type of plant: anthocyanins are contained in chokeberry (50 mg%), black currants (610 ... 920 mg%), cherries (250 ... 330 mg%); leukocyans - in sea buckthorn (240. ..260 mg%), apples, rowan; catechins are found in large quantities in apples, rowan. The presence of polyphenols in pectin extracts due to enzymatic oxidation reactions leads to darkening of both the extracts and pectins. The presence of some flavonoids (naringin in citrus) and terpenoids (in citrus) causes a bitter taste of fruits and products of their processing, including pectin extracts.

Pectin-containing raw materials contain and extract organic acids: the most common malic (0.7 ... 1.3%) in apples; citric - 1% in currants, 5.7% in lemons; tartaric (0.3 ... 1.7%) is in the grapes. Their content in raw materials determines its acidity. Active acidity (pH) for fruits is pH = 3 ... 4, for vegetables pH = 4.5 ... 6. Acidity determines the taste and affects some technological processes: hydrolysis, gelation, sterilization, etc. The presence of acids in liquid and dry pectin extracts causes a sour taste, increases shelf life.

Vitamins contained in plant raw materials have different qualitative and quantitative composition, even for plants of the same species. However, in the technological processing of raw materials are destroyed and contained in pectin extracts in small quantities.

Extraction of pectin is accompanied by the extraction of macronutrients (K, Ca, Mg, Fe, P, S, Na) and trace elements (Cu, Mn, Mo) from plant raw materials. They are distributed unevenly in the fruit. Thus, the core of apples contains several times more Ca, K, Mg and P than the pulp, so their content in pectin extract will be higher than in juices. Some of the macro - and microelements are contained in plants in the form of salts of organic acids (phytates, oxalates, etc.). Some Ca^{2+} and Mg^{2+} ions are part of protopectin and are released during hydrolysis, passing into pectin extract. The amount of minerals in the product determines the ash content, which in the pectin extract is 0.1 ... 1.0%. The ash content in pectin and pectin products determines the effectiveness of the purification of pectin extracts and pectin.

At the same time, the organoleptic characteristics of pectin extracts (taste, smell) from fruit raw materials improve with increasing degree of extraction of cell juice from raw materials, which allows to use them as a beverage, as well as for the production of blended beverages for general use. At the same time the nutritional value of products increases.

Chemical composition and organoleptic characteristics of pectin extracts

The nutritional and biological value of pectin extracts and dietary products based on them is determined by their chemical composition. Studies of the chemical composition of pectin extracts obtained under industrial conditions have shown that they contain, in addition to pectin, carbohydrates, organic acids, crude protein and other substances (table 1.7).

Pectin extracts are a homogeneous viscous liquid that has a sour, characteristic taste and smell from raw materials, from light gray, yellow to brown colour. The main physicochemical parameters are presented in table. 1.8.

The quality indicators of dry pectin extracts obtained by drying concentrated extracts in a spray dryer are presented in table.1.9.

Table 1.7

Chemical composition of pectin extracts

Indicators	Apple extract	Beet extract	Citrus extract
Mass fraction of pectin substances, %	0,88	0,71	0,95
Mass fraction of sugars, %	1,07	0,91	1,28
Mass fraction of "crude" protein, %	0,19	0,16	0,12
Organic acids, % in terms of citric acid	0,32	0,17	0,55
Vitamins	traces	traces	traces

Table 1.8

Physico-chemical parameters of pectin extracts

Indicators	Apple		Citrus		Beet		Carrot	
	Extract	Concentrate	Extract	Concentrate	Extract	Concentrate	Extract	Concentrate
Mass fraction of soluble solids, %	2,0	6,0	1,8	6,5	1,7	6,6	2,7	7,3
Mass fraction of pectin, %	1,0	3,0	1,2	3,6	1,1	3,5	1,5	3,1
pH	3,0	3,0	3,5	3,5	2,5	2,5	2,8	2,8
The strength of 2% pectin gel by the method of Sosnowski, kPa	53	53	50	50	40	40	30	30
Complexing ability, Pb^{2+}/ml	0,95	1,7	0,8	1,5	3,1	6,6	2,5	2,9

Table 1.9

Quality indicators of dry pectin extracts

Indicators	Extracts		
	Apple	Beet	Citrus
Mass fraction of moisture, %	9,2	9,0	9,4
Mass fraction of pectin, %	41,9	43,2	36,5
PH of 5% solution	3,0	2,8	3,4
Saccharose, %	12,4	10,8	10,8
Mass fraction of "crude" protein, %	7,03	8,3	9,8
Gelling ability, kPa	35,9	20,6	37,2
Complexing ability, mg Pb^{2+}/ g of extract	35,6	153,0	25,6

Mineral and amino acid composition of pectin extracts. Extraction of pectin is accompanied by the extraction of micro- (Cu, Mn, Zn) and macronutrients (K, Ca, Mg, Fe, Na) from plant raw materials. They are distributed unevenly in plants. Thus, the core of apples contains several times more Ca, K, Mg than the pulp, so their content in pectin extract will be quite high. Most of the micro- and macronutrients are contained in plants in the form of salts of organic acids (eg, sodium phytate). A number of Ca ions are part of protopectin [31, 32, 33] and are released during hydrolysis, turning into pectin extract. The amount of minerals in the product determines the ash content, which ranges from 0.1% to 0.3% by weight of dry pectin extracts.

The content of macro-, microelements, as well as the content of heavy metal ions in dry beet, apple, carrot extracts are given in table. 1.10, 1.11.

Table 1.10

Mineral composition of dry pectin extracts

Pectin extract	Macro-, microelements, mg/100 g						
	Mg	Ca	K	Na	Fe	Mn	Cr
Beet	0,20	21	25	9	38	0,0005	0,8
Apple	0,15	8,6	136	18	62	0,0005	0,64
Carrot		15	40	25	54	0,0006	0,30

Table 1.11

The content of heavy metals in pectin extracts

Name of extracts	The content of heavy metal ions, mg/kg				
	Zn^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Hg^{2+}
Pectin (permissible by	30,0	1,0	10,0	0,1	0,1
Beet pectin extract	2,0	0,7	5,6	0,02	0,02
Apple pectin extract	2,0	0,9	1,2	0,04	0,01
Carrot pectin extract	0,6	0,8	0,4	0,01	0,02

Apple, carrot pomace and beet pulp contain a significant amount of amino acids [15, 16]. In addition, amino acids are formed in the process of hydrolysis of protein substances of pectin-containing raw materials. The amino acid composition of dry pectin extracts was determined (table 1.12).

Table 1.12

Amino acid composition of pectin extracts

The name of the amino acid	Pectin extracts, mg-10/100 mg		
	Beet	Apple	Carrot
lysine	20,76	3,12	4,36
histidine	7,99	1,22	1,11
arginine	8,22	1,25	1,67
oxyproline	25,49	—	—
aspartic acid	17,21	18,01	13,66
threonine	14,09	3,45	4,66
serine	15,49	5,98	5,14
glutamic acid	28,50	13,30	28,64
proline	17,08	2,78	5,13
glycine	11,63	4,89	6,19
alanine	13,46	5,38	7,82
cysteine	1,58	1,12	0,26
valine	13,80	1,9	3,94
methionine	1,01	0,64	0,40
isoleucine	4,76	1,43	3,83
leucine	10,20	3,83	5,87
tyrosine	13,97	1,74	2,26
phenylalanine	6,33	2,81	2,17

Amino acid-enriched pectin extracts have a high biological value, and make it possible to use them in the production of food and biologically active additives.

Apple concentrate technology

In order to organize a comprehensive processing of apples and expand the range of pectin-containing canned products, pectin concentrate technology is of greatest interest to increase the profitability of enterprises for processing fruits and vegetables and raw materials [17, 18, 19, 21].

There are various schemes for producing pectin concentrate using sulfite, lactic, tartaric, citric, orthophosphoric acids or electroactivated water as a hydrolytic factor [5].

Dried and fresh apple pomace is used as a raw material. Preparation of the pomace consist in grinding them to a size of 1.5...2.0 mm and washing with water with a temperature of 20...25 °C within 20...30 min [57].

Hydrolysis of extraction of pectin substances is carried out at the following parameters: temperature - 80...90 °C, pH = 2,8...3,2; the ratio of the mass flow rates of the solid and liquid phases of 2.5...4.0; the duration of the process is 1.0...1.5 hours.

After hydrolysis, the mixture is separated by pressing, decantation and the like. The pectin extract is cooled, clarified, filtered and directed to the concentration to a pectin content of 2.5...3.0 %, followed by aseptic storage.

In enterprises where there are no conditions for aseptic storage, the extract is treated in sulfitators; storage is carried out in enameled containers for 6...9 months.

The concentrate can also be preserved with sorbic acid or its salts (sorbate of potassium or sodium). To do this, at a temperature of 80 °C bring in sorbic acid in an amount of up to 0.1% by weight. Stir for 10...15 min, then the concentrate is cooled to a temperature of 20 °C and sent for storage. The concentrate can be preserved by hot bottling in an airtight glass container.

The technological scheme of production of apple pectin concentrate is shown in fig. 1.3.

Liquid pectin technology

The following pectin-containing raw materials are used for the production of liquid pectin: apple pomace, beet pulp, fruit and vegetable pomace. Various acids are used as hydrolyzing substances: citric, orthophosphoric, lactic, etc.

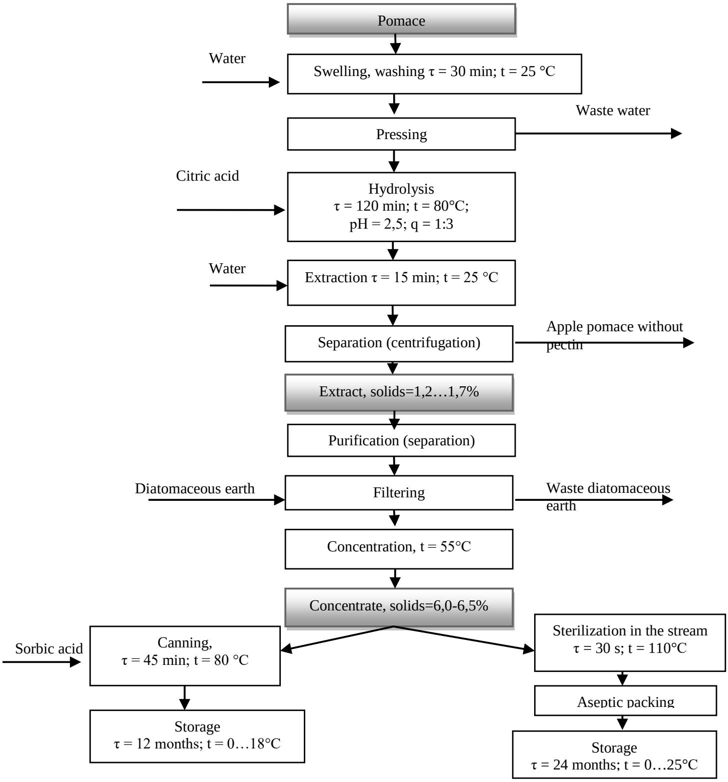


Fig. 1.3. Technological scheme of pectin concentrate production from apple pomace

Investigation of the process of enzymatic deesterification for obtaining low-esterified pectins

The effect of enzymes on pectin. The breakdown of pectin by enzymes is of great practical importance and is widely used in the processing of sugar beet fruit, as well as in the clarification of juices and wines. As is known, under the action of enzymes of the hydrolase class, the reactions proceed according to the following scheme:

$$RR1 + H\text{-}OH \leftrightarrow RH + R1OH.$$

In the process of enzymatic hydrolysis, an enzyme-substrate complex is formed, which undergoes intramolecular rearrangement under the influence of the active center of the enzyme. The rupture of the anhydride bond of the catalyzing substrate leads to the release from the enzyme-substrate complex of one of the reaction products. The second product is released after rearrangements associated with the addition of a water molecule. In the process of enzymatic hydrolysis of pectin substances involved: pectinesterase, endopolygalacturonase, exopolygalacturonase [35, 62].

Non-hydrolytic cleavage of pectin is channeled by enzymes from the class of pectintranseliminase lyases. Pectolytic enzymes are widespread, they are synthesized by plants, microorganisms, but are absent in animal cells. According to the report of the Commission for the development of enzymes nomenclature, pectolytic enzymes are classified as follows [63].

Pectinesterase (polymethylgalacturonatesterase, enzymes classification (EC) 3.1.1.11) deesterifies pectin with the formation of pectic acid due to the removal of methoxyl groups. Pectinesterases are synthesized by higher plants, microscopic fungi and bacteria. They have a high specificity to the methyl ester of pectic acid. With the gradual demethoxylation of pectin, there is a marked decrease in enzyme activity. Pectinesterase of fungal origin has a high activity at pH 5.0 ... 6.5 and a temperature of 50 ° C for 60 • 60 s.

Endopolygalacturonase (EC 3.2.1.15) hydrolyzes α- (1-4) -bonds of pectic acid in an arbitrary, disordered manner. The enzyme is produced by microorganisms and higher plants. With increasing degree of esterification of pectic acid, the degree and rate of hydrolysis decrease, due to the fact that free carboxyl groups increase the activity of the enzyme. The activity of the enzyme decreases with decreasing chain length of oligogalacturonans.

Exopolygalacturonase (EC 4.2.2.9) hydrolyzes pectin, sequentially cleaving bonds from the unreduced end of the substrate. Fungal exopolygalacturonases show maximum activity at pH 4 ... 6 and form monogalacturonic acid as the final product. The bacterial enzyme from *Erwinia aeroideae* acts at pH 7.2 and the product of catalysis is digalacturonic acid.

There is information about endopolymethylgalacturonase, which hydrolyzes α-(1-4) - pectin bonds. But the existence of this enzyme has not been conclusively proven: there is a possibility that polymethalacturonase is taken as polygalacturonase drugs that contain pectinesterase.

In addition, if the substrate is not completely esterified, the possibility of hydrolysis of pectin by polygalacturonase or polygalacturonate lyase in areas that do not contain methoxyl groups is not excluded.

The class of lyases that act on pectin substances include endo- and exopolygalacturonatelyase, polymethylgalacturonatelyase.

Endopolygalacturonatelyase (EC 4.2.2.2) performs a disordered, arbitrary cleavage of pectic acid bonds in the transelimination reaction. The optimal pH value = 8.0 ... 10.0. One of the main features of pectolyticlyases is their activation by calcium ions.

Exopolygalacturonatelyase (CF 4.2.2.9) sequentially cleaves pectic acid from the unreduced end of the substrate molecule in the transelimination reaction. For these enzymes, the optimal pH values = 8.0 ... 9.5.

Endopolymethylgalacturonatelyase causes arbitrary cleavage of pectin during transelimination. It is the only known enzyme that directly hydrolyzes pectin. The main producers are fungi and a small number of bacteria. Depending on the producer, the pH optimum effects of enzymes range from 5.5 to 8.3. The best substrate for endopolymethylgalacturonatelyase is highly esterified pectin. Polygalacturonic acid and pectic acid amide are not hydrolyzed by the enzyme. Endopolymethylgalacturonatelyase activity decreases rapidly with decreasing chain length.

Pectolytic enzyme preparations are widely used in food industries for maceration of plant raw materials, reduction of viscosity of juice concentrates, clarification of juices, etc.

For pectin production it is important to prevent the action of factors of enzymatic destruction of pectin substances. For the preparation of pectin-containing raw materials it is possible to use enzyme preparations released from pectolytic enzymes.

Enzymatic method of obtaining low-esterified pectin (LEP) is based on the specific action of the enzyme pectinesterase, which catalyzes the hydrolysis of ether bonds of pectin [22, 23, 24, 25, 26].

Obtaining LEP having a molecular weight close to the molecular weight of native pectin, determines the choice of source of pectinesterase with a minimum content of polygalacturonase complex, the result of which is the rupture of L-1,4-bonds in the polyuronide molecule. In plants, polygalacturonase is rare and in small quantities, so many foreign companies offer highly purified and homogeneous pectinesterase preparations from plant raw materials, despite the fact that its release from plants is complicated by strong adsorption by plant tissues. So the firm Sigma (USA) offers different types of pectinesterase preparations from tomatoes and oranges. However, due to the limitations of the raw material base, plants cannot be industrial sources of enzymes. In addition, pectinosterases of plant and microbial origin differ in their properties and mechanisms of action.

Microbial pectinesterases are more thermostable than plant ones. The optimal pH value of pectinesterases of higher plants is in the alkaline zone in the range from 7 to 9, fungal - in the acidic range from 3.5 to 7.

A fast and easily controlled method of obtaining apple LEP involves the concentration of pectin extract simultaneously with the deesterification of tomato pectinesterase. Comparative studies of fungal and plant pectinesterases have been conducted abroad. They convincingly show the benefits of fungal esterases. It is emphasized that samples of pectins de-esterified by fungal pectinesterases, as well as samples of pectins de-esterified by alkali, have a uniform distribution of charge density of free carboxyl groups and are characterized by the degree of counterion binding, which increases with increasing charge density.

In samples of pectin deesterified by plant pectinesterases, the degree of binding of Ca^{2+} ions was independent of the degree of esterification. The reason for this is the lateral distribution of free carboxyl groups, due to which dimers are formed.

Analysis of pectin deesterification methods shows that the undeniable advantage of the alkaline deesterification method is the high reaction rate. However, given the fact that the alkaline deesterification rate of depolymerization increases with increasing temperature faster than the rate of deesterification, to obtain high-quality samples of LEP requires careful control of temperature and pH. But even with all the process parameters set depending on the composition of the processed material, the degradation of the pectin macromolecule cannot be avoided and the pectin obtained by alkaline deesterification is characterized by a lower molecular weight compared to the original.

Caustic alkalis in the process of deesterification act not only as a catalyst, they are spent on the neutralization of carboxyl groups released. In this regard, to maintain the speed of the process at a constant level requires continuous additional application of alkali. In addition, significant amounts of acids are required to neutralize the reaction mixture and remove pectin-bound ions. All this leads to a significant increase in the cost of reagents compared to other methods of deesterification. The main disadvantage of the acid method of reducing the degree of esterification is the low speed of the deesterification process.

The product of acid deesterification differs in its structure from pectin obtained using alkalis. In an acidic environment, the glycosidic bond in the galacturonide molecule is much more stable than the glycoside bond of neutral polysaccharides included in the pectin molecule. As a result, in acid hydrolysis the bonds between the polyuronide chain and the branches of neutral saccharides that are part of the pectin macromolecule are destroyed. At the same time, the accompanying neutral polysaccharides undergo hydrolysis [13, 39, 40].

The most promising way to reduce the degree of esterification of pectin is the use of microbial pectinesterases. The pectins obtained with their use are devoid of the disadvantages characteristic of pectins obtained by plant pectinesterases and due to the lateral arrangement of free carboxyl groups. Currently, the widespread use of enzymatic hydrolysis to reduce the degree of esterification of pectin is hindered by the lack of industrial preparations of microbial pectinesterase, which have sufficient purity, as well as the lack of detailed ideas about the processes of enzymatic deesterification.

A study of the enzymatic de-esterification of apple pectin using the enzyme preparation of the company DSM (Netherlands) (Fig. 1.4).

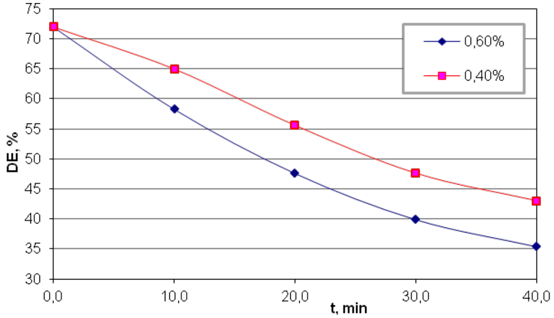


Fig. 1.4. Dependence of changes in the degree of esterification of pectinon the duration of the enzymatic deesterification process (concentration of enzyme preparation 0.4%, 0.6%)

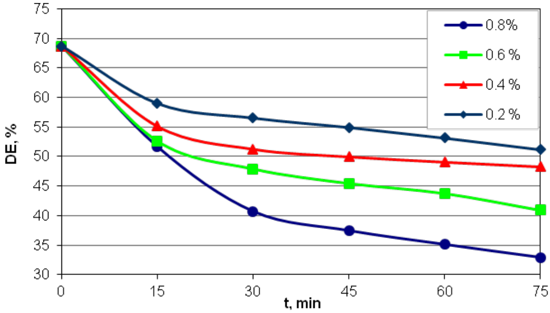


Fig. 1.5. Dependence of changes in the degree of esterification of pectin on the concentration of the enzyme preparation of pectinesterase

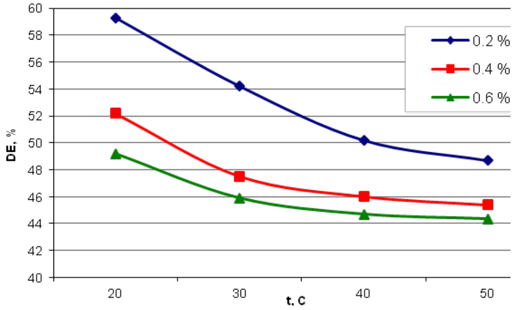


Fig. 1.6. Dependence of the degree of esterification of pectin on the temperature of the deesterification process

Technological scheme of liquid pectin production

Technological scheme of liquid pectin production includes the following stages (Fig. 1.7):

Washing of raw materials. Pectin-containing raw materials from the warehouse enters the shop and is loaded into the washing tank with a stirrer. Washing is carried out with drinking water with a temperature of 20… 25 ° C at a ratio of raw materials and water of 1: 3 for 30 minutes, after which it is fed to the belt press by a screw mezgon pump.

Pressing. The raw material is fed to the belt press, where the wash water is removed from the raw material to a solids content 25… 28%, by auger conveyor is fed into the storage tank.

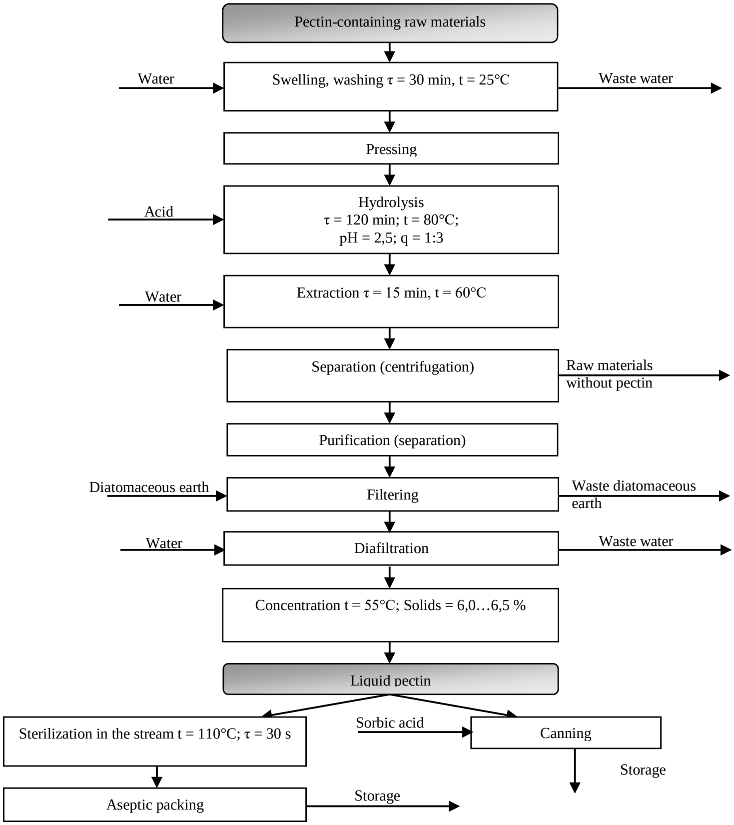


Fig. 1.7. Technological scheme of production of liquid pectin

Hydrolysis-extraction. The process of hydrolysis of protopectin and extraction of pectin substances is carried out in a hydrolyzer with a stirrer.

Hydrolysis-extraction of pectin substances is carried out with periodic stirring with the addition of acid solution to the raw material (at a ratio of 1: 3).

At the end of loading the reagents, the hydrolyzer is sealed and the process of hydrolysis-extraction of pectin substances is carried out at the following parameters:

pH = 2.5… 3.2; process temperature 75… 80 ° C; the ratio of pomace and acid solution is 1: 3; duration of hydrolysis-extraction process 120 min.

After the hydrolysis-extraction process, the mass is pumped to the separation centrifuge.

Separation of hydrolysis mixture. To separate the extract, the hydrolysis mixture is fed to a continuous centrifuge. After centrifugation and removal of pectin, the raw materials are sent for neutralization with further use as cattle feed, and the pectin extract is sent to the tank. Qualitative indicators of pectin extract after centrifugation: solids content - 1,2 ... 1,7%; content of PS (pectin substances) - 0.5%; pH = 2.8… 3.2.

Separation of pectin extract. The pectin extract from the tank is pumped into a separator for cleaning. The sediment formed as a result of separation is sent for disposal. The clarified extract from the separator is fed into the tank, and then pumped to the diatomaceous earth filter.

Extract filtration. The process of filtering the pectin extract is carried out on a diatomaceous earth filter. The filtered extract is sent to the tank.

Concentration of the extract. The extract is concentrated on a vacuum evaporator to a solids content = 6.0… 6.5%, the concentration of precipitated pectin substances 2.5… 3.5%, the pH of the extract is 1.7… 2.2. Concentration takes place at 55 ° C for 2 hours. The vacuum on the vacuum evaporator is formed by the condensing head. The extract is evaporated under vacuum. After evaporation, the liquid pectin enters the tank, where it is pumped for aseptic preservation or preservative preservation.

Preservation of liquid pectin with sorbic acid. From the vacuum evaporator, pectin is fed into a tank with a stirrer and a jacket with a usable volume of 10 m^3. The estimated (0.05… 0.1%) amount of sorbic acid is added to pectin. The mixture is stirred for 45 minutes until complete dissolution of the preservative. The liquid pectin is then fed into a storage vessel, having previously cooled it in a heat exchanger.

Packing of liquid pectin in an aseptic installation. The concentrate is sterilized in a stream for 30 s at a temperature of 110 ° C and packed in plastic bags, which are placed in plastic or metal barrels with a volume of 200 liters.

The role of pectin in dairy production. The group of pectins for the dairy industry includes pectins with different degrees of esterification, which have a constant (standardized) value of susceptibility to calcium in milk, as well as well-established rheological properties. In particular, the dairy industry uses special pectins to stabilize the structure and extend the shelf life of various dairy products, such as liquid yogurts, puddings, etc. In addition, pectins, as components of fruit and jelly fillers, sauces and liquid concentrates, can be used in the production of fruit yogurts, fruit-dairy desserts with fruit fillers.

The properties of dairy products, such as pH, calcium ion concentration, protein and sugar content, especially affect the structure-forming properties of pectins. The main indicators that determine the nature of the action of pectins in dairy products are the degree of esterification and the degree of dissociation of molecules.

The nature of the stabilizing effect of pectins. After mixing a solution of highly esterified pectin with neutral milk, for a short time, it can be seen the formation of a flaky precipitate of milk proteins, which include casein. At the end of the reaction, the protein flakes together with the smallest droplets of fat form a viscous, thick emulsion, over which is a layer of whey. This process is reversed and does not lead to chemical changes in the composition of casein molecules. In the first scientific publications such a reaction was called the "pectin phenomenon of milk". The method of protein precipitation by pectin has been used previously, for example, in cheese production. Currently, this technology has no industrial significance.

In neutral milk at pH 6.6, casein molecules carry a negative charge and, as a result, repulsive forces predominate between them. This prevents protein deposition. It is assumed that pectin as a strong hydrophilic compound destroys the protective hydrate shell of casein (Fig. 1.8), as a result, the stability of the latter deteriorates sharply.

When the pH of milk decreases, casein molecules gradually lose negative charges. At the isoelectric point (determined pH value of the product, for casein 3.6) is established almost equal ratio between positive and negative charges. The molecule loses its hydrate shell and at a pH value below the isoelectric point acquires a total positive charge [61, 62].

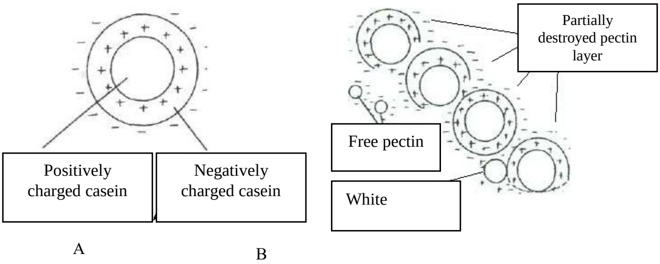


Fig. 1.8. Stabilizing effect of pectin on dairy products

A-stabilized casein particle; B - unstable sediment

Negatively charged highly esterified pectins when mixed with a fermented milk product, such as yogurt, interact electrostatically with casein molecules that carry a total positive charge. The formed casein-pectin complex acquires an excessive negative charge with a predominance of repulsive forces between molecules. As a result, the interaction of proteins with each other is excluded, as well as the formation of sediment and the separation of whey. The product acquires the so-called physical stability.

Pectins used to stabilize fermented milk products, such as liquid yogurt, must have a high molecular weight and a precise degree of esterification - within 70%, as pectins with a lower degree of esterification are able to react with calcium in milk, and pectin molecules with more with a high degree of esterification have fewer negatively charged carboxyl groups and are therefore less reactive. The dosage of pectin depends on the content of milk proteins. Optimal dosage does not affect the viscosity of the product, pectin overdose impairs taste.

An important factor that ensures the stability of the product is the pH value 4. Lowering the pH by 0.5 units leads to a sharp decrease in stability. Thus, the pH values of fermented milk products and their acidity significantly affect the dissociation of pectin and, consequently, its ability to interact with calcium ions.

When low-esterified pectins are added to neutral milk, a milk pudding or gel is formed, the consistency of which can vary from viscous-fluid to strong, depending on the dosage of pectin. Such structures are formed as a result of the interaction of pectin with calcium in milk. It is assumed that the gelling effect is enhanced in the process of additional interaction of pectins with milk proteins.

Low esterified pectin for neutral dairy products must meet certain requirements. First of all, it must be standardized with respect to the constant value of sensitivity to calcium ions. The commercial pectin preparation must also contain a certain amount of suitable buffer salts.

When using LEP in the production of fermented milk products, such as yogurt with a stable structure, it can be increased the strength of milk jelly and prevent the release of whey. It should be borne in mind that as a result of lowering the pH in the process of acidification of yogurt, general changes in salt balance lead to the complete transition of calcium compounds into soluble form. Thus, the concentration of calcium ions reacting with pectin increases sharply. The formed calcium pectate precipitates.

Therefore, the high concentration of calcium limits the amount of pectin used. If the dosage of pectin in the product still needs to be increased, the excess activity of calcium ions is reduced by adding buffer substances and, if possible, simultaneously increase the pH.

The process of stabilization of dairy systems is influenced by the following factors:

The pH value of the product. Most fermented milk products have a pH value of 3.8…4.0. Pectins have a stabilizing effect in the pH range of 3.5…4.2. Optimal organoleptic properties of the product can be achieved when working in the pH range of 3.6…4.0. Therefore, in the case of the use in the recipe of yogurt with low protein content of a large amount of fruit juice, it is necessary to pre-determine the total (titrated) acidity of the juice. To prevent a decrease in the stability of the product, ie the separation of whey, it is recommended to use fruit juices, the acidity of which is equal to or greater than the acidity of yogurt.

At pH values below 3.5 pectins can not stabilize the product. This is due to a sharp decrease in the degree of dissociation of carboxyl groups of pectin at pH below 3.5, which, in turn, reduces the degree of interaction of pectin with casein molecules. At pH above 4.0, the stabilizing effect is also reduced. It is not recommended to work at pH above 4.2, which in some cases can lead to an undesirable increase in viscosity due to the increased degree of dissociation of pectin molecules.

The amount of pectin used to stabilize the dairy product is also affected by the acidity of fruit juice (if used). Fruit juice with a low total acidity adversely affects the stability (there is a risk of whey separation) of the finished product. To correct this negative effect, it is needed to increase the dose of pectin.

Milk protein content. It has been empirically established that for satisfactory stabilization of yogurt from milk with a protein content of 4%, it is sufficient to use 0.5% pectin in terms of weight of finished yogurt. At higher concentrations of milk proteins it is necessary to increase the dosage of pectin by the appropriate amount.

In cases of low milk protein content, it is possible to reduce the dosage of pectin, which may be disproportionate to the concentration of milk protein. So, for example, it is established that at 1% content of milk proteins the minimum admissible level of dosing of pectin from 0,15% to 0,25% is reached.

Particle size of milk proteins. In the process of microbiological acidification of milk (maturation, cultivation of yogurt) a number of technological parameters determine the particle size of milk proteins. As noted above, the stabilizing effect is achieved by adsorption of pectin on the surface of milk proteins. Adsorbed pectin gives all particles a single electrostatic charge, which leads to repulsive forces between individual particles.

For optimal stabilization of milk protein particles with very small sizes, more pectin is required in order to bind a significant area of adsorption of the protein surface. At the same time, very large protein particles also require a significant amount of pectin to keep them in equilibrium (suspended).

Increasing the dosage of pectin can be carried out to a level of 0.7% in terms of weight of the finished product.

Products "Pektolin", "Pektolakt" and beverage "Pektynovyi". Technologies and recipes of dairy products with the addition of pectin, produced on the basis of secondary raw milk, have been developed. Their organoleptic characteristics are given in table 1.12.

Table 1.12

Organoleptic characteristics of dairy pectin products "Pektolin", "Pektolakt" and beverage "Pektynovyi"

Indicator	Characteristic		
	"Pektolin"	"Pektolakt"	"Pektynovyi"
Appearance and consistency	Homogeneous liquid with a broken or intact clot, slight viscosity and slight whey separation are assumed	Homogeneous liquid-drink, with the consistency of kissel, the system - dessert	Homogeneous liquid-drink
Taste and smell	Pure sour-milk with taste and aroma of filler	Sweet and sour, whey with the taste and aroma of the filler	Sweet and sour, whey with the taste and aroma of the filler
Color	Creamy, uniform throughout the mass	Light brown, uniform throughout the mass	Characteristic of the filler

"Pektolin" is made from skim milk or buttermilk and pectin concentrate. Pasteurized milk raw material and prepared pectin concentrate are mixed and fermented with a leaven consisting of separately cultured mesophilic lactic acid streptococcus, acidophilic bacillus and kefir leaven. Fermentation is carried out at a temperature of 32±2 °C to a clot acidity of 85 °T. The duration of fermentation is 6...8 hours. At the end of fermentation, the product is cooled, mixed and packaged in consumer containers.

The basis of "Pektolakt" is a mixture of whey with skim milk and pectin concentrate, to which sugar and starch are added. The filtered whey and skim milk are pasteurized and cooled. Starch is dissolved in chilled skim milk. The whey is mixed with pectin concentrate, heated to 65...70 °C, added granulated sugar, heated to 90 °C and added the dissolved starch. The mass is incubated for 5...0 minutes. Thoroughly mixed and cooled product is packaged.

The recipe of the beverage "Pektynovyi" includes whey, pectin, sugar and aromatic additives. Pectin is thoroughly mixed with sugar in a ratio of 1:1, poured the prescribed amount of water at a temperature of 40...45 °C and left for 3...4 hours to swell the pectin, stirring the mixture periodically. Then filtered whey is introduced into the mixture with stirring, heated to a temperature of 90 °C, added a filler (syrup), cooled and served for bottling [63, 64].

Sour milk paste "Lali" (TS U 18019595-30-96) is made from pasteurized skim or normalized milk by fermentation with yeast and subsequent separation of whey with the addition of pectin, salt, spices and greens to the protein base. Depending on the mass fraction of fat, "Lali" pasta is made low-fat, 2.5; 5.0; 10.0% fat. The leaven is prepared using pure cultures of thermophilic lactic acid bacteria. The milk is fermented for 4...6 hours to obtain a clot with an acidity of 80...90 °T. Pressing takes place at a temperature of 8...12 °C to a mass fraction of moisture 80...89 % depending on the fat content of the final product. Fillers are added to the pressed paste [65, 66].

The product has a sour-milk sharply salty taste with a hint of spices, garlic, greens. Due to the preservative properties of salt, as well as the presence of pectin and spices in the product, the guaranteed shelf life of "Lali" paste is 10 days.

1.3 Prospects of using plant protein products in technology of thermostable dairy-containing fillings

1.3.1 Features of production technologies of plant protein products

Protein-oil crops are the most common food ingredient. For receiving in the technological purposes of raw materials from protein-oil crops it is obligatory their preliminary preparation during which the by-product is a hard shell - the husk and in some places the seed coat, and the main raw material – protein flour, groats, concentrates and isolates. For receiving groats and protein flour, the oilseeds are pre-degreased, cleaned and crushed. The resulting flour has a protein content of 40 to 50%. The protein concentrate has a slightly higher protein content of 65 to 70%. The peculiarity of its preparation is to remove simple and complex carbohydrates, mineral salts and other water-soluble substances from fat-free flour. The highest protein content has the isolate – more than 90%. This amount of protein is caused primarily by its purification from non-protein substances [209; 235 ; 258]. Among these raw materials of protein-oil crops protein concentrates differ in inexpensive and not labor-consuming production process. Oil from seeds and kernels of oilseeds is removed without chemical treatment by two methods: cold and hot pressing. The method of cold pressing consists in the gentle temperature influence (about 50 °C) on the raw material during its pressing. The final product is characterized by almost unchanged composition of all nutrients, especially protein. During hot pressing, which is characterized by the influence of high temperatures – 100 ... 120 °C, the resulting final product can not only have a much lower content of nutrients and modified protein by the given temperature influence, but also can be burned slightly. Therefore, it is advisable to use the method of cold pressing for preservation of useful substances, during which the cake is 45%, and the amount of protein in it varies from 50 to 70%, fat - about 10%, i.e. approaching to concentrates by protein content [208; 223; 235].

1.3.2 Prospects of plant protein concentrates production and substantiation of the expediency of using sesame seed concentrate in the technology of thermostable dairy-containing fillings

In the food industry, a large interest in leading scientists is caused by such protein-oil crops as peanuts, sunflowers, sesame, rapeseed and soybeans. They have a high content of polysaccharides, unsaturated fatty acids, proteins and fats [224; 258; 291; 297]. Of these cultures, the most labor-intensive technological preparation process is characterized by soybeans [53; 231]. It also adversely affects the human body: causes various diseases, such as Alzheimer's disease, infertility, impairs physical development, and its content of trypsin and chymotrypsin inhibitors in the amount of about 6% prevents cleavage of proteins in a small intestine [82; 192].

Unlike soybeans, peanuts are the most promising raw material widely used in food. It is characterized by high functional and technological properties and balanced and complete protein composition [7; 53; 130; 192; 231 ; 297].

Peanuts contain from 45 to 60% of high-quality edible oil, 30...35% of complete protein with a high content of essential amino acids, 18...20% of carbohydrates, vitamins A, D, E, B1, B2, PP, E.

80% of peanut oil consists of unsaturated fatty acids, the use of which significantly lowers the level of cholesterol in the blood. The high content of tocopherols gives peanuts antioxidant properties. After a special short-term heat treatment, the kernels of peanuts are more easily freed from the skin, which is rich in coarse dietary fibers that prevent the breakdown of not only proteins, but also starch. Products obtained from peanuts include: flour, paste, protein and lipid-protein isolates.

Peanut oil is used in the margarine and canning industry. Oil production waste in the form of peanut pomace is used during the production of halva.

Particularly popular is peanut paste, which has the appearance of a paste-like mixture of ground, peeled peanuts with the addition of peanut oil, sugar and various additives that ensure a stable consistency of the product. It was determined that the use of protein peanut mass in the production of food products contributes to the improvement of the properties of the recipe components contained in them.

No less popular raw material is sesame, which is not inferior to peanuts in terms of functional and technological properties and chemical composition.

The value of sesame seeds is determined by the content of its nutrients and their physiological properties. Sesame seeds contain fats (44 – 58%), proteins (18 – 25%), carbohydrates (13.5%) and ash [4]. Its composition includes such vitamins as: beta-carotene, thiamin, riboflavin, niacin, pyridoxine, α- and γ-tocopherols, as well as choline and mineral compounds of calcium, potassium, phosphorus, magnesium, manganese, iron, copper and selenium. Sesame is considered the richest source of calcium, because the consumption of only 30 g of sesame provides 40% of the daily need for it. Sesame seed proteins are characterized by high biological value. They are rich in methionine, and especially tryptophan. However, sesame seed proteins are limited in lysine, although to a lesser extent than wheat proteins. In terms of solubility in the group composition of sesame seeds, salt-, water-, and alkaline-soluble proteins prevail [5]. Research on the effect of sesame protein products on animals showed a decrease in the level of cholesterol, triglycerides and lipoproteins in their blood serum [6], and the mechanism of action of sesame proteins affects blood serum lipids in a similar way to soy proteins.

Sesame seeds contain up to 60% of one of the best edible plant oils, which is classified into the oleic-linoleic acid group, since it contains almost equal proportions of monounsaturated oleic (35-48%) and polyunsaturated linoleic (37-48%) fatty acids, and also about 10% of saturated fatty acids - stearic and palmitic. The high content of linoleic acid and dietary fiber in sesame seeds ensures its ability to reduce the level of cholesterol in human blood plasma [7]. Other fatty acids are contained in small amounts, in particular, the content of linolenic fatty acid, which is indispensable in nutrition, is 0.2%. Sesame oil, compared to others, has better preventive properties against high blood pressure, high blood cholesterol and lipid peroxidation, increasing the content of enzymatic and non-enzymatic antioxidants in the body [8]. These properties of sesame oil are ensured both by the content of monounsaturated oleic acid and by the content of other biologically active components, in particular phytosterols, tocopherols and lignans [16]. According to some scientists, the main functional ingredients of sesame and sesame oil are lignans: sesamin, sesamolin, sesaminol and a small amount of sesamol [9]. Due to their presence, as well as the content of γ-tocopherol, sesame oil has high oxidative stability. Sesame lignans contribute to the normalization of cholesterol levels in the blood, increase in the bioaccumulation of vitamin E (γ-tocopherol), high antioxidant protection, and provision of estrogenic activity [10].

Given the chemical composition of protein-oil crops (Table 1.13), it is likely that the resulting products of their processing will have a similar tendency to change the chemical composition, in particular in concentrate (Table 1.14).

Table 1.13

Comparative characteristics of the chemical composition of protein-oil crops

Name of crop	Fat, %	Protein, %	Carbohydrates,%	Ash,%	Energy value, kcal
Rapeseed seeds	43,6	30,8	7,2	4,5	544,4
Sesame seeds	48,7	19,4	12,2	5,1	562,9
Sunflower seeds	52,9	20,7	10,5	2,9	600,9
Peanut kernel	45,2	26,3	9,9	2,6	551,6

Table 1.14

Characteristics of the chemical composition of protein-oil concentrates

Product name	Fat, %	Protein, %	Carbohydrates,%	Energy value, kcal
Rapeseed concentrate	6	48	8	278
Sesame seed concentrate	6	52	6	286
Sunflower seed concentrate	10	46	8	306
Peanut kernel concentrate	7	56	8	319

Based on the above characteristics of the chemical composition, it should be noted that the most promising raw material by the amount of protein and fat is rapeseed, and energy value - sesame seeds, which is inferior to sunflower seeds. However, the concentrates of these protein-oil crops are characterized by a slightly different chemical composition (Table 1.13). Thus, from the data table. 1.8 revealed that the highest protein values are characteristic of peanut kernel concentrates. Closer to it by the protein content, but somewhat lower in fat content, is a sesame seed concentrate.

Therefore, in order to provide thermostable dairy-containing fillings of new organoleptic, technological, physicochemical and structural-mechanical properties, it is advisable to include in their prescription composition the product of processing protein-oil crops - sesame seed concentrate.

1.4 Expediency of freezing application and influence of the technological regimes on quality of thermostable dairy-containing fillings

Thermostable dairy-containing filling belongs to the category of products that cannot retain their quality for a long time, therefore apply freezing to extension of expiration dates, that represents one of ways of conservation. In turn, conservation prevents destruction, spoilage and keeps the product in an invariable look. Both domestic and foreign scientists have been engaged in maintaining the quality of food and studying the impact of low-temperature storage on the change and prolongation of food quality. Nowadays, a great contribution has been made by the scientific school of Kharkiv State University of Food Technology and Trade Doctor of Technical Sciences, Professor Potapov V.A. - “Research of heat and mass transfer processes and refinement of apparatus for heat and refrigeration processing of foodstuffs” and the scientific school of Odessa National Academy of Food Technologies Doctor of Technical Sciences, Professor Lagutina A.Yu. - "Heat exchangers of cooling systems and condenser units of refrigeration units". It is known that, under normal storage conditions, in the temperature range 0… 4 °C, biochemical, physico-chemical, microbiological changes in food are slowed down. However, in the analysis of the works of domestic scientists, it was found that there is a group of bacteria - psychrophils, capable of continuing their activity at relatively low temperatures, namely from 10 to -10 °C [26; 119; 139; 229]. For this reason, it is advisable to use the freezing process to extend the shelf life of the filling.

Products subjected to freezing must retain their taste, nutritional and quality properties after defrosting and during storage at low temperatures. All foods contain water - bound and free. Freezing affects the speed of the flow of biochemical processes and the intensity of microorganisms development, as well as causes a change in the thermophysical and mechanical properties of the product and leads to a change in the phase state of water, turning it into ice, accompanied by migration of moisture in the product [3; 5; 18; 74; 119; 139; 219]. The formation of ice crystals occurs in an intercellular substance, in which as the freezing of water begins to increase the amount of soluble substances. The emergence of a difference in osmotic pressure, that is, a change in concentrations between cells and in cells, leads to the formation of a flow of moisture from cells to crystals in the intermediate space [18; 35; 171; 219]. Such moisture migration results in significant changes in the structure of the product: cell deformation, partial rupture of cell membranes, and so forth.

The formation of ice crystals in food is due to a decrease in cryoscopic temperature, as opposed to isothermal crystallization of pure water [41; 151]. The decrease in cryoscopic temperature in a product depends on the amount of water and the substances that form solutions with it [24; 211; 212]. The decrease in temperature occurs with increasing concentration of the solution due to the freezing of water and lasts until the system reaches the eutectic point at which it freezes at a constant composition [3; 18; 24; 25]. The formation of crystalline germs, the rate of diffusion of water molecules and heat removal of crystallization all contribute to the rapid growth of crystals. In the case of lowering the temperature to about 0 ° C, the growth rate of the crystals is insignificant, and the diffusion of water molecules is mainly affected. If to reduce temperature further, the heat transfer speed will begin to influence and the crystal growth rate will reach maximum and with achievement of speed of freezing that higher than the speed of diffusion it falls [24; 59; 65; 119; 139].It is known that the filling structure depend on the size of the ice crystals. This indicates that the main criterion for freezing temperatures (Table 1.15), which affects the size and uniformity of the distribution of ice crystals, is the speed of crystallization. It is determined by the intensity of refrigerant supply and the rate of heat removal [3; 24; 26; 136; 179; 219].

Table 1.15

Characteristics of freezing modes

Freezing	Temperature condition	Moisture characteristics	Note
Slow	$t = –10…–12^{o}$ C, v = 1 cm/g	Large ice crystals: d = 0,5 mm, L = 10 mm	The destruction of the structure
Fast	$t = –18…–20^{o}$ C, v = 5–10 cm/g	Fine crystalline ice structure: d = 5 microns, L = 0,1 mm	Maintaining structure
Superfast	t over $–40^{o}$ C, v over 10 cm/g	Small ice crystals: d = 20…230 nm, L = 0,1 mm	The destruction of the structure

Storages of a product at low temperatures not only preserves its physicochemical properties, but also leads to a decrease in a significant number of microorganisms, which depends on the intensity and speed of the temperature decrease. The highest number of microorganisms dies during fast freezing at temperatures of –18… –20 °C, and the smallest - during slow shallow freezing in the temperature range –10… –12 °C [112; 222; 244]. It should be noted that after defrosting the product, the microorganisms that have not died during freezing begin to develop, therefore during defrosting it is necessary to avoid additional moisture. If the defrosting is carried out at high temperatures (20 ... 25°C), there is an intensive reproduction of microorganisms, it less reproduce - during slow defrosting (1 ... 8°C) [38; 44; 59; 84; 119; 139]. It is widely recognized today the technology of rapid low-temperature freezing of the product, during which the movement of moisture decreases during ice formation, as well as defrosting with the use of air or liquid. Therefore, the rational freezing temperature is –16… –20 °C (fast freezing). During fast freezing, the largest number of microorganisms dies, slowing down the course of biochemical processes.

2 Scientific substantiation of the thermostable filling technology using dairy raw materials and sesame seed concentrate

2.1 Study of functional and technological properties of hydrocolloids

During the research of modern production technologies of foodstuff the leading scientists pay great attention to hydrocolloids or their compositions. This attention is due to the fact that hydrocolloids have different origin, chemical composition, structural-mechanical and functional-technological properties; and thanks to this, it has wide functional action. As this paper deals with topical issues of creation of thermostable gel-like (condensed and structured) products, it is advisable to first pay attention to those recipe components that determine the thermostable and structural-mechanical properties of finished products - starch and pectin. The study of functional and technological properties of these hydrocolloids of different nature will allow to establish their suitability for further use in the composition of thermostable fillings.

The thermostable properties and specific structural framework of the filling depend mainly on the ability of the hydrocolloids to bind and hold moisture. Also, since the product under development has fat components, its properties depend on the ability to bind and hold fat. So, it is necessary to begin researches on studying the functional and technological properties of hydrocolloids - to study their moisture-holding ability and ability to hold fat (MHA, AHF) [2; 207; 238].

It is known that due to the formation of a negative charge on the surface of the hydrocolloid, the particle repels, encountering a charged particle, which characterizes the hydrophilic-hydrophobic properties [2; 17; 60; 207; 238; 241; 295]. In view of this assertion, fats and oils are used to impart certain properties to the fillings, which necessitates studies to examine the relationship between MHA and AHF. The MHA was determined at the following range of hydrocolloid swelling temperatures: 20 ± 2°C, 40 ± 2 °C, 60 ± 2 °C and 80 ± 2 °C. Table 2.1 shows the results of the study of MHA and AHF of widespread pectins and starches in Ukraine.

Table 2.1

Comparative characteristics of MHA and AHF of hydrocolloids

Raw materials	Indicator				
	MHA,%				AHF, %
	20±2^{0} C	40±2^{0} C	60±2^{0} C	80±2^{0} C	
Apple pectin highly esterified	65±3,0	84±4,0	40±2,0	38±1,0	32±1,5
Citrus pectin highly esterified	38±1,5	80±4,0	74±3,5	63±3,0	20±1,0
Apple pectin low-esterified	145±7,0	183±9,0	101±5,0	89±4,0	28±1,0
Citrus pectin low-esterified	165±8,0	210±10,5	125±6,0	105±5,0	65±3,0
Corn starch	44±2,0	62±3,0	85,5±4,0	–	42±2,0
Potato starch	40,5±2,0	60±3,0	60±3,0	–	46±2,0
Corn starch modified	46,5±2,0	72±3,5	93±4,5	–	61±3,0

From the table 2.1 shows that with increasing temperature up to 60 °C, the MHA of all studied starches increases, and at temperatures above 60 °C, the study is impossible. This tendency of change indicates the swelling of their starch grains due to the absorption and holding of moisture through chemical interaction. The intensity of increase MHA observed at temperatures above 40 °C indicates the beginning of the process of starch gelation, that is formation of colloidal systems with a certain spatial configuration [22; 150; 241].

On the other hand, for pectins the index of MHA changes quite unevenly. From the table 2.1 shows that the MHA of pectin increases rapidly with increasing temperature from 20 ± 2 to 40 ± 2 °C, and decreases in the temperature range from 40 ± 2 to 80 ± 2 °C. Such an uneven change MHA of the pectin is probably due to the fact that the hydrogen bonds between their molecules occur at temperatures from 20 ± 2 to 40 ± 2 °C, and with subsequent increase in temperature over 40 ± 2 °C, they partially break down and release moisture [193; 205, 241].

Thus, in the conducted researches on the studying MHA of starches and pectins it was found that the highest rates of MHA have corn starch modified (93% at 60 ± 2o C) and low-esterified citrus pectin (210% at 40 ± 2o C). In view of this, it can be concluded that it is expediency to use of corn starch modified and citrus low-esterified pectin as a prescription component of thermostable filling.

It is known that to give the fillings of high thermostable and structural-mechanical properties, a mixture of different hydrocolloids wich having a synergistic effect is introduced into their composition [216; 246]. Therefore, in order to study the possibility of joint use of corn starch modified and low-esterified citrus pectin, functional and technological properties of mixtures of these hydrocolloids were investigated (Table 2.2).

Table 2.2

Comparative characteristics of MHA and AHF of mixtures of “low-esterified pectin citrus : corn starch modified”

Low-esterified citrus pectin: corn starch modified, %	Indicator				
	MHA,%				AHF, %
	20±2^0 C	40±2^0 C	60±2^0 C	80±2^0 C	
0,8:1,0	126,5±5,0	132±6,5	174±8,5	192±9,5	82±4,0
0,8:2,0	155±7,5	176±8,5	191±9,0	238±11,5	91±4,5
1,0:0,8	150±7,0	195±9,5	142±7,0	95±4,5	72±3,5
2,0:0,8	194±9,5	220±11,0	164±8,0	103±55,0	79±3,5

From the data table 2.2 shows that in mixtures where corn starch modified predominates, there is a gradual increase in the indicators of MHA, and where low-esterified pectin citrus is dominated, on the contrary - a decrease of MHA with increasing temperature. Higher rates of MHA under conditions of temperature rise have a mixture with a concentration of modified corn starch 2.0% and low-esterified citrus pectin 0.8%. According to scientific data [193], such changes of MHA contribute to the aggregation of hydrophilic molecules of pectin and starch. Components of starched paste which consisting of a branched chain of amylopectin and amylose molecules interact via hydrogen bonds with a spiral chain of pectin molecule, forming a common three-dimensional spatial grid [107; 193; 242; 249; 256; 261; 293]. This indicates a synergistic effect and the ability to further share corn starch modified and low-esterified citrus pectin in the production of thermostable filling. Therefore, high functional and technological parameters, prove the synergistic effect of the joint use of a mixture of pectin citrus low-esterified concentration of 0.8% and corn starch modified concentration of 2.0%.

Moving on to further research, it should be noted that one of the main conditions for the realization of a number of properties of low-esterified pectins is the presence of divalent metal ions - Ca2 +. In this case, the source of calcium ions was calcium citrate salt, insoluble in water. To convert calcium citrate from crystalline to soluble state, it is necessary to lower the pH of the water medium. The most common and readily available citric acid was used to reduce the pH.

Investigating the rheological and technological properties of systems with different ratios of components and concentrations of low-esterified pectins, it is worth paying attention to the content of calcium citrate concentration of 0.02, 0.04 and 0.06% - in accordance with established standards, which do not contradict sanitary and hygienic examination [47; 81; 111; 184; 286].

2.2 Investigation of rheological properties of hydrocolloids

2.2.1 Investigation of the effective viscosity of hydrocolloids

The main technological function of pectin and starch in the process is the adsorption and holding of moisture by various forms of communication, which helps to increase the viscosity due to the rapprochement of particles in the food system [116; 193]. The viscosity of hydrocolloid systems, in turn, depends on the location and number of hydrophilic groups along the chains and characterizes the consistency of the finished product; it also depends on the temperature and the components additionally introduced to the hydrocolloids.

It is known that starch, depending on the concentration in the system is capable of forming a viscous suspensions, and pectin - gels. It is also worth paying attention to the dehydration property of sugar: it is known that with the addition of sugar to the "water-starch" system (to a certain concentration) the viscosity, the speed of starch gelation and the strength of the starch paste begins to decrease. This is due to the interference of sugar in various interactions and connexion. It is able to exhibit its properties at 200 C (to bind and hold about 8 - 12 water molecules), and starch - only with increasing temperature [116; 174; 185; 228; 243; 296].

Given the analytical data on low-esterified pectins, in particular their functional-technological and rheological properties, the proposed introduction of dry substances to the new thermostable filling is about 55% [36; 47; 107; 111; 185; 242; 249; 256; 261; 275; 285; 293]. The dependence of the effective viscosity of the "sugar-water-starch" system on various types of the most common starch and pectins on temperature is shown in Fig. 2.1 - 2.3.

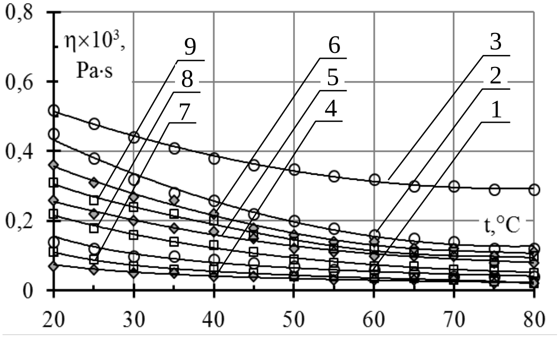
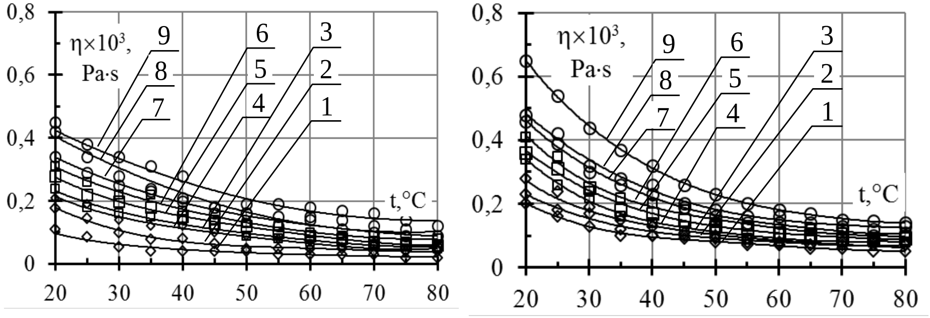


Fig. 2.1. Dependence of effective viscosity of starch paste on temperature at 55% sugar concentration and starch: 1, 2, 3 – potato starch 1,0, 2,0, 3,0% in accordance, 4, 5, 6 – corn starch 1,0, 2,0, 3,0% in accordance, 7, 8, 9 – corn modified starch 1,0, 2,0, 3,0% in accordance

In Fig. 2.1 there is a gradual decrease of effective viscosity with increasing temperature. This is due to the fact that the starch begins to absorb a large amount of moisture with increasing temperature, which causes the formation of a starch paste, and with a decrease in temperature becomes a viscous mass due to the fixation of intermolecular bonds. Possibly that the introduction of sugar into the "water-starch" system causes abnormal viscosity characteristics - a decrease of effective viscosity with increasing temperature. This indicates the ability of sugar to "intercept", "delay" moisture and thus increase the point (temperature) of the transition of starch grains to starch paste [174; 185; 228; 243; 296].

In Fig. 2.2 presents the research results of dependence of effective viscosity of apple and citrus low-esterified pectin on temperature influence

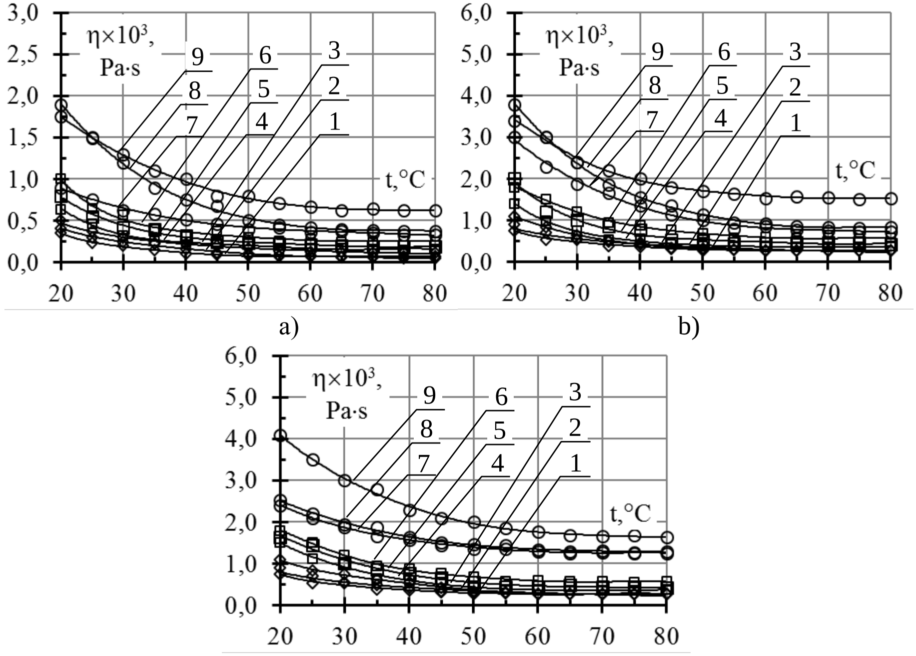


a) b)

Fig. 2.2. Dependence of effective viscosity of the system "pectin low-esterified: calcium citrate" at a sugar concentration of 55% and a) apple pectin b) citrus pectin on temperature (%): 1 – 0,50:0,02; 2 – 0,80:0,02; 3 – 1,10:0,02; 4 – 0,50:0,04; 5 – 0,80:0,04; 6 – 1,10:0,04; 7 – 0,50:0,06; 8 – 0,80:0,06; 9 – 1,10:0,06

According to the data (Fig. 2.2), the "sugar-water-pectin low-esterified-calcium citrate" system shows a slight decrease of the effective viscosity of citrus and apple pectin with increasing temperature. It is revealed that the effective viscosity increases with increasing in content of pectin and calcium citrate. Thus, the increase of the reactive groups leads to the formation of new groups, which further form a gel grid [36; 47; 111; 275; 285]. When comparing the effective viscosity of a pectin in the system sets minimum and maximum temperature limits of changing its values. The temperature difference of system of the citrus pectin is about 7 ºC lower than the apple pectin . Therefore, lowering the temperature causes emergence of hydrogen communications and grouping of molecules, which leads to gel formation, growth of viscosity and strength. [107; 185; 242; 249; 256; 261; 293].

By comparing the effective viscosity curves (Fig. 2.2), it was determined that the highest effective viscosity had the apple low-esterified pectin. The lower viscosity at which the consistence of smaller density is formed characteristic of citrus low-esterified pectin. Therefore, in order to provide plastic consistency and stable physico-chemical and technological properties under the influence of the action of high temperature, pectin was combined with modified corn starch (Fig. 2.3).



a) b)

c)

Fig. 2.3. Dependence of effective viscosity of the system "corn starch modified: calcium citrate" at a sugar concentration of 55% and citrus low-esterified pectin (%): a) 0,5, b) 0,8 and c) 1,1 on temperature (%): 1 – 1,00:0,02; 2 – 2,00:0,02; 3 – 3,00:0,02; 4 – 1,00:0,04; 5 – 2,00:0,04; 6 – 3,00:0,04; 7 – 1,00:0,06; 8 – 2,00:0,06; 9; 3 – 3,00:0,06

As can be seen from the data of Fig. 2.1, corn modified starch is characterized by a not very high effective viscosity concerning a system with potato starch and not sufficiently low compared to the same corn starch system.

Data of Fig. 2.3 indicate an increase of effective viscosity in the "sugar-water-pectin-starch-calcium citrate" system with increasing pectin concentration, corn starch modified and calcium ions. With the increase in the content of corn starch modified, it becomes a more viscous, more plastic consistency.

From the results of the researches (Fig. 2.3) it can be concluded that the most expedient in the technological aspect indicators of effective viscosity varies from $1{,}68\times10^{-3}$ to $1{,}43\times10^{-3}$ Pa·s in the temperature range 18… 25 ˚C that is, the "sugar-water-pectin-starch-calcium citrate" system with citrus low-esterified pectin 0.80%, modified corn starch 3.00% and calcium citrate 0.04%.

2.2.2 Determination of changes in the strength of hydrocolloids

The peculiarity of the technological aspect of the use of hydrocolloids (pectin and starch) in food products, in particular in thermostable fillings, is based on their ability to form a characteristic strong structure. However, certain conditions and time are required to form the filling structure.

It has been found that, in process of cooling ofthe various types of pectin and starch to a temperature of 20 ± 2 ° C, with endurance in a current 24 × 602 s systems of varying strength are formed for . The results of the study of the strength of the pectins structure and mixtures of pectin and starch are shown in Fig. 2.4 and 2.5. It is worth noting that strength studies for low-esterified pectin at concentrations of 0.5 and 0.8% are not possible due to the formation of a system of rather low strength. It is also difficult to determine the strength of starch paste due to the low concentration of starch in the suspension and the formation of very weak starch paste

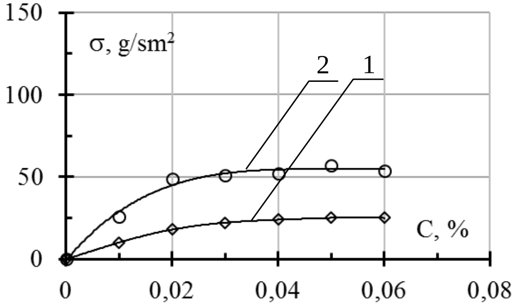


Fig. 2.4. Dependence of the strength of low-esterified pectins gels at concentrations of 1.1% with sugar content 55% from the concentration of calcium citrate:1 - apple pectin; 2 - citrus pectin

In Fig. 2.4 shows the increase in the strength of low-esterified pectins gels , provided that the concentration of calcium citrate is increased. It has been found that apple pectin gels with the addition of divalent metals (calcium citrate) have too weak and dense structure compared to citrus pectin gel, which will further complicate the formation of the filling. It is believed that in terms of general structural properties, in particular strength, the best indicators for further use in the filling production process are the gel of low-esterified pectin with a content of calcium citrate from 0.04 to 0.06%.

The dependence of the gel strength of the low-esterified pectins and modified corn starch mixture on the concentration of divalent metals is shown in Fig. 2.5. The strength indicators are given for low-esterified pectin of concentrations 0.8 and 1.1% and modified corn starch - 3.0%; at lower concentrations too weak gels are formed. The strength indicators of these gels has a similar tendency to change the strength of the above gels of low-esterified pectins (Fig. 2.4).

Thus, from the data of Fig. 2.5 shows that the gel strength of a mixture of pectin and starch increases with increasing concentration of ingredients, namely pectin (apple and citrus) low-esterified and calcium citrate.

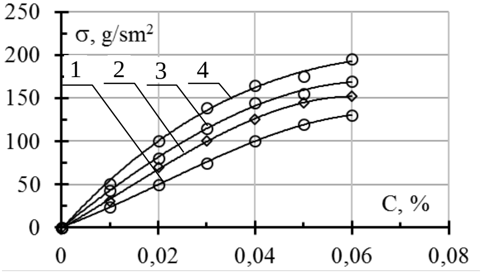


Fig. 2.5. Dependence of the gel strength of a mixture of low-esterified pectins and modified corn starch with sugar content of 55% on the concentration of calcium citrate in the ratio of "apple pectin:starch",%: 1 - 0,8: 3,0; 2 - 1.1: 3.0; "citrus pectin:starch",%: 3 – 0,8:3,0; 4 – 1,1:3,0

It is also seen that the gel strength of the mixture of citrus pectin low-esterified and modified corn starch higher with the content of apple pectin. It is proved that the addition of starch to pectin helps to increase the strength of the investigated gels, giving them a softer and gentler structure than those that do not contain its (Fig. 2.4). As a general conclusion from the results of the study of the hydrocolloids strength (Fig. 2.4 and 2.5) it should be noted that the highest strength values has a gel mixture of citrus low-esterified pectin and modified corn starch

2.3 Investigation of the thermostable properties of hydrocolloids

The above-mentioned results of the study of functional-technological and rheological properties of a number of hydrocolloids are the basis for further experimental studies in order to introduce them into the recipe composition of the thermostable filling that is being developed. Therefore, for the logical and complete justification of the use of hydrocolloids in the technology of thermostable product it is advisable to study the thermostable characteristics of these hydrocolloids.

2.3.1 Melting temperature change of hydrocolloids

It should be noted that due to the low concentration of modified corn starch and the presence of sugar in the slurry, it is not possible to measure the melting point since a rather low viscosity system is formed. Therefore, the change in melting point is given for low-esterified pectins with the addition of calcium citrate salt (Fig. 2.6).

In Fig. 2.6 shows an increase in melting temperature with increasing concentrations of apple and citrus low-esterified pectins. During the comparison of temperature data it is proved that apple low-esterified pectin is characterized by higher melting point relative to citrus low-esterified pectin. It should be noted that the formed gel of these pectins with the content of calcium citrate is characterized by insufficient plasticity, so in order to provide new and improve these characteristics was introduced modified corn starch.

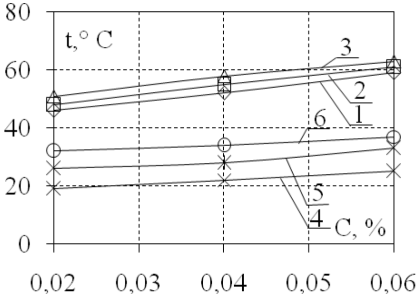
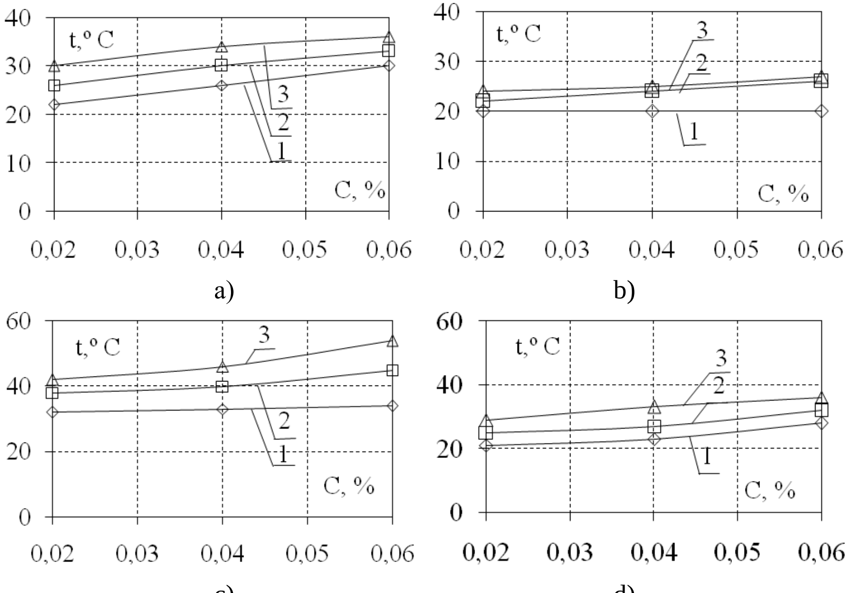


Fig. 2.6. Dependence of the melting point of gels of low-esterified pectins on the concentration of calcium citrate with a sugar content of 55%, low-esterified apple pectin (%): 1 – 0,5; 2 – 0,8; 3 – 1,1, and low-esterified citrus pectin (%): 4 – 0,5; 5 – 0,8; 6 – 1,1

In the case of the combination of apple and citrus low-esterified pectin concentration of 0.50% with modified corn starch of concentration of 1.00, 2.00 and 3.00% and the addition of calcium citrate of 0.02, 0.04 and 0.06%, a gel with high fluidity at room temperature (20 ± 2° C) is formed, which is not appropriate for use in thermostable fillings. Thus, the study of the change in the melting point of the gels of a mixture of pectins and starch was carried out at concentrations of apple and citrus pectin 0.80 and 1.10% (Fig. 2.7).

Data of Fig. 2.7 indicate a slight change in the melting point of the pectin experimental gels. It was found that the melting point of the gels increases with the concentration of the components. This is probably due to the fact that as the concentration of these components increases, the number of free strong bonds between them increases - a spatial grid is formed, which more resistant to high temperature [36; 47; 111; 107; 242; 249; 256; 261; 275; 285; 293].



a) b)

c) d)

Fig. 2.7. Dependence of the melting point of gels of low-esterified pectins on the concentration of calcium citrate with a sugar content of 55% in the ratio: a) «apple pectin: modified corn starch» (%): 1 – 0,8:1,0; 2 – 0,8:2,0;3 – 0,8:3,0; b) «citrus pectin: modified corn starch» (%): 1 – 0,8:1,0; 2 – 0,8:2,0; 3 – 0,8:3,0; c) «apple pectin: modified corn starch» (%): 1 – 1,1:1,0; 2 – 1,1:2,0; 3 – 1,1:3,0; d) «citrus pectin: modified corn starch» (%): 1 – 1,1:1,0; 2 – 1,1:2,0; 3 – 1,1:3,0

However, with the addition of starch, there was a slight decrease in the melting point of the gels of the pectin-starch mixture. This change is most likely due to the regrouping of the low-esterified pectin bonds formed in the gel and the emergence of new free ones, which require the additional involvement of calcium-containing raw materials to form a grid with high temperature properties. It should be noted that the formed gel of this mixture of pectin and starch is characterized by a softer and plastic consistency than the gel with only pectin.

Thus, based on the results of the data obtained from the study of the melting point, we can conclude that the combined organoleptic properties and melting point, it is rational to use a gel containing low-esterified citrus pectin 0.80%, modified corn starch 3.00% and calcium citrate 0.04%.

2.3.2 Change of thermal stability of hydrocolloids

The duration of thermal stability is characterized by the ability to maintain a stable form and general physicochemical properties throughout the period of temperature action. Indicator of thermal stability of pectins and a number of pectin and starch mixtures are given in Table. 2.3.

It is established that as a result of the addition of calcium citrate, the formation of too weak gels of apple and citrus pectin is observed, which with a temperature rise above 20 ± 2 ° C quickly pass to the liquid state, and therefore difficult to determine their thermal stability. Starch suspensions are also quite difficult to determine, due to its low concentration and sugar content. This is due to the high ability of sugar to dissolve in water, which causes the dehydration of starch polymers and the formation of layers of concentrated solutions in the starch paste, which leads to a decrease in viscosity [174; 185; 228; 243; 296]. It is advisable to investigate the change in the duration of thermal stability of mixtures of pectins and modified corn starch. It should be noted that at concentrations of the studied low-esterified pectins 0.50%, modified corn starch 1.00, 2.00 and 3.00% and calcium citrate 0.02, 0.04 and 0.06% are formed gels of considerable fluidity at room temperature. Thus, the study of thermal stability began with a concentration of low-esterified pectins of 0.80% (Table 3.3).

Таблиця 2.3

Comparative characteristics of the thermal stability of mixtures "low-esterified pectin: modified corn starch"

Raw materials, %	Indicators											
	Thermal stability $\tau \times 60^{-1}$, s, at a temperature											
	40±2° C			60±2° C			80±2° C			100±2° C		
	C (calcium citrate), %											
	0,02	0,04	0,06	0,02	0,04	0,06	0,02	0,04	0,06	0,02	0,04	0,06
low-esterified apple pectin : modified corn starch												
0,8:1,0	0,51±0,03	1,33±0,07	2,37±0,10	0,47±0,02	1,19±0,06	1,58±0,08	0,41±0,02	0,30±0,02	1,11±0,06	0,14±0,01	0,17±0,01	0,30±0,02
0,8:2,0	0,53±0,03	2,31±0,10	3,41±0,20	0,52±0,03	2,12±0,10	2,58±0,10	0,37±0,02	1,30±0,07	1,52±0,08	0,36±0,02	0,41±0,02	1,08±0,05
0,8:3,0	0,57±0,03	3,48±0,20	5,37±0,30	0,58±0,03	2,42±0,10	3,08±0,20	0,50±0,03	1,50±0,08	2,14±0,10	0,42±0,02	0,45±0,02	1,27±0,06
1,1:1,0	1,54±0,08	2,00±0,10	2,50±0,10	1,10±0,06	1,50±0,08	2,50±0,10	0,47±0,02	0,50±0,03	1,30±0,07	0,17±0,01	0,29±0,01	0,43±0,02
1,1:2,0	11,50±0,60	21,00±1,00	30,0±1,00	1,50±0,08	2,20±0,10	3,00±0,20	0,50±0,03	1,45±0,07	2,15±0,10	0,41±0,02	1,20±0,06	1,30±0,07
1,1:3,0	21,00±1,00	30,0±1,50	30,0±1,00	2,25±0,10	2,55±0,10	3,10±0,20	1,40±0,07	2,10±0,10	2,40±0,10	0,55±0,03	1,30±0,07	2,08±0,10
low-esterified citrus pectin : modified corn starch												
0,8:1,0	0,23±0,01	0,58±0,03	1,36±0,07	0,14±0,01	0,30±0,02	1,15±0,06	0,10±0,01	0,18±0,01	0,50±0,03	0,05±0,01	0,11±0,01	0,27±0,01
0,8:2,0	0,35±0,02	1,15±0,06	2,25±0,10	0,24±0,01	0,36±0,02	1,52±0,08	0,18±0,01	0,29±0,01	1,31±0,07	0,08±0,01	0,15±0,01	0,42±0,01
0,8:3,0	0,41±0,02	2,13±0,10	3,15±0,20	0,36±0,02	0,43±0,02	2,38±0,20	0,26±0,01	0,38±0,02	2,02±0,10	0,12±0,01	0,28±0,01	1,10±0,06
1,1:1,0	1,24±0,06	1,52±0,08	2,20±0,10	0,18±0,01	0,49±0,02	1,26±0,06	0,16±0,01	0,35±0,02	1,10±0,06	0,08±0,01	0,13±0,01	0,36±0,02
1,1:2,0	9,45±0,50	15,0±0,80	29,0±1,50	1,19±0,06	1,55±0,08	2,32±0,10	0,25±0,01	1,28±0,06	2,02±0,10	0,12±0,01	0,29±0,01	0,51±0,03
1,1:3,0	19,16±1,00	30,0±1,50	30,0±1,50	2,06±0,10	2,13±0,10	2,50±0,10	0,38±0,02	1,56±0,08	2,20±0,10	0,32±0,02	1,05±0,05	1,50±0,08

The data analysis of the table. 2.3 indicates an increase in the thermal stability of the gel of apple low-esterified pectin relative to citrus low-esterified pectin. The tendency of increase of thermal stability is revealed due to interaction of molecules of pectin with calcium. In this pectin molecules are crosslinked by calcium ions to form a spatial grid of pectin, which holds all the ingredients together [36; 47; 111; 107; 242; 249; 256; 261; 275; 285; 293].

Thus, based on the results of thermostable properties studies , which do not contradict the findings of the studies on the functional-technological and rheological properties of hydrocolloids, it is proved that the concentration of low-esterified citrus pectin is 0.80% with a concentration of 0.04% citrate. It has also been found that the additional content of modified corn starch (1.00 and 3.00%) is a prerequisite, since a soft and plastic consistency gel is formed with its participation. The values close to effective have a gel at low-esterified citrus pectin concentrations of 0.80%, modified corn starch 3.00% and calcium citrate 0.04%.

2.4 Investigation of functional and technological properties of protein concentrates of oilseeds

Today, the role of functional and technological properties of powdered raw materials (particle size of about 50 microns) obtained during the technological processing of plant protein oil crops, and water as a solvent in the process of food production has not been sufficiently studied [4; 13; 41]. However, due to the ability to control the physicochemical, structural, mechanical and technological properties, these studies are indispensable for the production of high-quality thermostable filling. Therefore, it is advisable to study the functional and technological properties of the selected plant additive - sesame seed concentrate, comparing the results of studies with the data on the functional and technological characteristics of other protein concentrates of oilseeds (Table 2.4).

Table 2.4

Comparative characteristics of MHA and AHF
of plant protein concentrates of oilseeds

Сировина	Indicator				
	MHA,%				AHF,%
	20±2° C	40±2° C	60 ±2° C	80 ±2° C	
Sesame seed concentrate	263±13,0	267±13,0	270±13,0	271±13,0	155±7,5
Sunflower seed concentrate	150±7,0	152±7,5	157±7,5	160±8,0	150±7,5
Flax seed concentrate	495±24,0	624±31,0	693±34,5	740±37,0	116±5,5
Peanut kernel concentrate	92±4,5	138±6,5	161±8,0	140±7,0	105±5,0
Walnut kernel concentrate	115±5,5	137±6,5	166±8,0	175±8,5	147±7,0

According to the table. 2.4 there was an increase in the indices of MHA of the investigation raw material in the temperature range from 20±2 to 80±2° C. Obviously, there is swelling of proteins and polysaccharides contained in the raw material; moisture is withheld mainly due to chemical interaction [4; 13; 34; 41; 61; 149; 208; 243; 297]. Due to the "protein-water" chemical interaction and a number of interactions of a non-chemical nature, a rather stable system is formed, MHA of which is almost independent of temperature.

Hydrophobic interactions of concentrates have a similar tendency to change properties. According to the data table. 2.2 it was found that the lowest values of AHF are characteristic for peanut kernel concentrate (105%) and the highest - for sesame seed concentrate (155%).

Considering the results of the conducted research, it can be concluded that sesame seed concentrate is functionally and technologically important component. It should be used as an ingredient that can bind and hold moisture and fat [61; 130; 174; 298].

2.5 Investigation of influence of high temperature on the technological properties of the research system of thermostable filling

2.5.1 Study of influence of recipe components on melting temperature of the research system of the thermostable filling

In order to prevent and correct changes of development, it is advisable to investigate its melting point with respect to the formulation composition. The dependence of the melting point of the experimental system of thermostable filling on the content of skimmed milk powder and the ratio "SMP: SSC" are shown (Fig. 2.8 and 2.9).

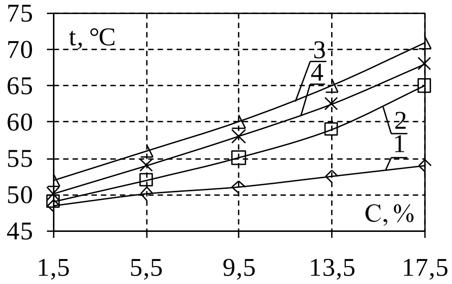


Fig. 2.8. Dependence of the melting point of the test system TF on the content of SMP at concentrations: 1 – low-esterified citrus pectin 0,8%; low-esterified citrus pectin and modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%

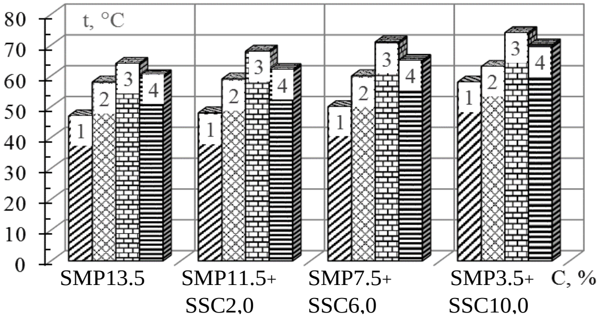


Fig. 2.9. ependence of the melting point of the test system TF on the content of SMP and SSC at concentrations: 1 – low-esterified citrus pectin 0,8%; %; low-esterified citrus pectin and modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%

In Fig. 2.8 and 2.9 show an increase in the melting temperature with increasing content of prescription components of calcium-containing (skimmed milk powder) and protein-polysaccharide nature (sesame seed concentrate) in the experimental system of TF. According to the above data, it was found that the lowest melting point (48.5 °C) to have an TF experimental system at low-esterified citrus pectin concentrations of 0.8% with a skimmed milk powder content of 1.5%. The highest value (71 °C) is characterized by the same pectin concentration of 0.8% and modified corn starch 3.0% with skimmed milk powder content of 17.5%, but this system is characterized by a rather dense structure. Less dense structure has a system with a given concentration of hydrocolloids and a dry skim milk content of 13.5%; the melting point is 65 °C. This phenomenon is due to the decrease in the number of free bonds of the carboxyl group of the pectin molecule [1; 236; 253; 278; 302].

Data Fig. 2.9 indicate the same above mentioned dependence of the melting point change. It has been found that in the experimental system of TF with increasing content of hydrocolloids and, in particular, plant protein additives - sesame seed concentrate - the melting point is increasing. From the obtained data it is determined that the rational concentrations of hydrocolloids and sesame seeds concentrate in the experimental system of TF are as follows: low-esterified citrus pectin - 0.8%, modified corn starch - 3.0%, skimmed milk powder - 7.5% and sesame seed concentrate - 6.0%.

2.5.2 Study of influence of recipe components on thermal stability of the research system of the thermostable filling

In order to further monitor changes in thermostable filling caused by the action of temperature, the dependence of the change of termal stability of the TF experimental system on temperature with different contents of the recipe components is shown (Table 2.5).

Таблиця 2.5

Comparative characteristics of thermal stability

C (modified corn starch), %	Thermal stability τ×60^{-1}, s, at a temperature													
	100±2^0 C		120±2^0 C		140±2^0 C		160±2^0 C		180±2^0 C		200±2^0 C		220±2^0 C	
	C (low-esterified citrus pectin), %													
	0,8	1,1	0,8	1,1	0,8	1,1	0,8	1,1	0,8	1,1	0,8	1,1	0,8	1,1
Skimmed milk powder 1,5%														
0	8,30±0,04	0	7,50±0,40	0	6,45±0,30	0	6,02±0,30	0	3,10±0,20	0	1,40±0,07	0	0,30±0,02	0
1,0	15,40±0,80	15,95±0,80	14,23±0,70	14,70±0,80	12,10±0,60	12,71±0,60	10,56±0,50	10,95±0,50	6,83±0,34	7,60±0,40	2,88±0,10	3,38±0,17	1,80±0,09	2,14±0,10
3,0	16,17±0,80	0	15,12±0,80	0	12,77±0,60	0	11,38±0,60	0	7,93±0,40	0	3,50±0,20	0	2,30±0,10	0
Skimmed milk powder 5,5%														
0	8,40±0,40	0	7,58±0,40	0	6,50±0,30	0	6,09±0,30	0	3,16±0,20	0	1,44±0,07	0	0,34±0,02	0
1,0	15,73±0,80	16,20±0,80	14,30±0,70	14,80±0,70	12,20±0,60	12,82±0,60	10,62±0,50	11,03±0,60	7,08±0,40	7,65±0,40	2,95±0,10	3,45±0,20	1,85±0,09	2,23±0,10
3,0	16,25±0,80	0	15,20±0,80	0	13,05±0,70	0	11,45±0,60	0	8,03±0,40	0	4,00±0,20	0	2,40±0,10	0
Skimmed milk powder 9,5%														
0	8,50±0,40	0	8,04±0,40	0	6,55±0,30	0	6,14±0,30	0	3,20±0,20	0	1,48±0,07	0	0,40±0,02	0
1,0	15,80±0,80	16,30±0,80	14,58±0,70	14,90±0,70	12,28±0,60	12,92±0,60	10,67±0,50	11,50±0,60	7,15±0,40	7,70±0,40	3,23±0,02	3,73±0,20	2,10±0,10	2,32±0,10
3,0	16,32±0,80	0	15,28±0,80	0	13,15±0,70	0	11,53±0,60	0	8,30±0,40	0	4,05±0,02	0	2,45±0,10	0
Skimmed milk powder 13,5%														
0	9,00±0,50	0	8,09±0,40	0	7,00±0,40	0	6,20±0,30	0	3,25±0,20	0	1,53±0,08	0	0,44±0,02	0
1,0	15,88±0,80	16,37±0,80	14,65±0,70	15,20±0,80	12,37±0,60	13,11±0,70	10,72±0,50	11,58±0,60	7,23±0,40	7,75±0,40	3,28±0,02	3,80±0,02	2,15±0,10	2,40±0,10
3,0	16,55±0,80	0	15,35±0,80	0	13,21±0,70	0	11,78±0,60	0	8,58±0,40	0	4,10±0,20	0	2,70±0,10	0
Skimmed milk powder 17,5%														
0	9,10±0,50	0	8,14±0,40	0	7,05±0,40	0	6,24±0,30	0	3,30±0,20	0	1,57±0,08	0	0,49±0,02	0
1,0	15,95±0,10	16,42±0,80	14,73±0,70	15,30±0,80	12,44±0,0,60	13,22±0,70	10,79±0,50	11,65±0,60	7,30±0,40	7,80±0,40	3,33±0,20	3,85±0,20	2,20±0,10	2,68±0,10
3,0	16,60±0,80	0	15,43±0,80	0	13,27±0,70	0	12,05±0,60	0	8,65±0,40	0	4,14±0,20	0	2,75±0,10	0
Ratio of “SMP:SSC” 11,5 : 2,0%														
0	9,5±0,50	0	8,12±0,40	0	7,05±0,40	0	6,60±0,30	0	3,50±0,20	0	2,00±0,10	0	0,55±0,03	0
1,0	16,0±0,80	16,70±0,80	15,00±0,80	15,85±0,80	12,50±0,60	13,65±0,70	11,00±0,60	11,85±0,60	7,70±0,40	8,50±0,40	3,50±0,20	4,00±0,20	2,50±0,10	2,70±0,10
3,0	17,0±0,90	0	16,05±0,80	0	13,89±0,70	0	12,15±0,60	0	9,25±0,50	0	4,50±0,20	0	3,10±0,20	0
Ratio of “SMP:SSC” 7,5 : 6,0%														
0	10,0±0,50	0	8,70±0,40	0	7,50±0,40	0	7,00±0,40	0	4,00±0,20	0	2,50±0,10	0	1,25±0,06	0
1,0	16,50±0,80	17,20±0,90	15,55±0,80	16,20±0,80	13,05±0,70	13,90±0,30	11,65±0,60	12,30±0,60	8,05±0,40	9,00±0,50	3,95±0,20	4,40±0,20	2,88±0,10	3,00±0,20
3,0	17,68±0,90	0	16,70±0,80	0	14,30±0,70	0	12,60±0,60	0	9,70±0,50	0	4,90±0,20	0	3,50±0,20	0
Ratio of “SMP:SSC” 3,5 : 10,0%														
0	10,40±0,60	0	9,10±0,50	0	7,95±0,40	0	7,20±0,40	0	4,50±0,20	0	3,20±0,20	0	1,55±0,08	0
1,0	17,20±0,90	17,80±0,90	15,90±0,80	16,70±0,80	13,80±0,70	14,40±0,30	12,40±0,60	12,70±0,60	8,70±0,40	9,50±0,50	4,45±0,20	4,70±0,20	3,30±0,50	3,85±0,20
3,0	18,10±0,90	0	17,50±0,09	0	14,90±0,70	0	13,20±0,70	0	10,40±0,50	0	5,20±0,30	0	3,65±0,20	0

According to the table. 2.5 there is a decrease in the thermal stability of the TF experimental system with increasing temperature. The thermal stability index of the TF system at a low-esterified citrus pectin of concentration 0.8% and a skimmed milk powder content of 1.5 to 17.5% at the lowest temperature effect (100 °C) varies from 8.3 to 9.1 × 60 s, respectively, at the highest (220 °C) - respectively from 0.3 to 0.49 × 60 s. The thermal stability index is slightly increased with the addition of modified corn starch , concentration of 1.0 and 3.0%. It follows that the indicator of thermal stability increases with the increase of modified corn starch and calcium-containing raw materials - skimmed milk powder in the system. A similar trend is observed in the case of partial replacement of skimmed milk powder with sesame seeds concentrate. It is revealed that the highest values of thermal stability are inherent in the TF experimental system at the concentration of low-esterified citrus pectin 0.8% and modified corn starch 3.0%.

Summarizing the data obtained for the partial replacement of skimmed milk powder with sesame seed concentrate, we note that the ratio of "SMP:SSC" as 7.5: 6.0% is rational in terms of organoleptic, consumer and technological qualities. In view of this, in the course of further experimental studies, attention should be paid to the revealed rational ratio of dairy raw material and plant protein supplement "SMP:SSC, as 7.5: 6.0%.

2.6 Investigation of moisture connection forms in the research system of the thermostable filling

2.6.1 Study of influence of recipe components on the moisture-holding ability of the research system of the thermostable filling

Moisture plays an important role in the production of thermostable fillings, because it determines the consistency, structure, duration of storage, etc. [13; 41; 149]. High MHA of thermostable fillings, in particular, contributes to the stability of organoleptic, physico-chemical, structural-mechanical and microbiological parameters during product storage. Of course, the recipe components of the filling, mainly hydrocolloids, have a great influence on the MHA. According to the results of studies of functional-technological, rheological and thermostable properties of hydrocolloids revealed that these properties are high in the case of a combination of low-esterified citrus pectin and modified corn starch. However, the change of MHA contributes to the introduction into the filling of other recipe components with hydrophilic properties, in particular skimmed milk powder and sesame seeds concentrate, which is a source of protein and calcium.

The features of the change of the MHA of the TF experimental system under the condition of partial replacement of skimmed milk powder with sesame seeds concentrate are shown in Fig. 2.10.

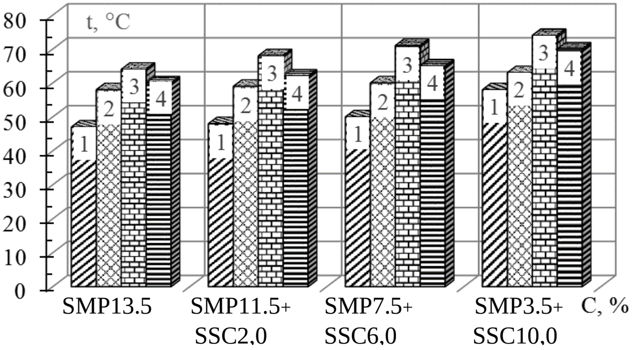


Fig. 2.10 Dependence of moisture-holding ability of the TF experimental system on the content of SMP and SSC and concentration: 1 – low-esterified citrus pectin 0,8%; low-esterified citrus pectin and modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%

From the above data of the TF research system (Fig. 2.10), taking into account the ratio of "SMP : SSC" and the concentration of pectin or composition with starch , there is a tendency to increase the MHA index with an increase in the system of components concentration (sesame seed concentrate, low esterified citrus pectin and mixture with pectin and modified corn starch). Taken together, these recipe components promote the entry into the research system of protein-polysaccharide nature substances , which in turn, are characterized by high adsorption and moisture-holding ability[4; 130; 149]. It is known that the hydrophilicity of individual proteins depends on their structure. Hydrophilic, amine and carboxyl groups present in the composition and located on the surface of the protein macromolecule attract the solvent molecules, strictly orienting them on the surface of the molecule [32; 160; 297; 300].

Summarizing the results of the MHA study of the TF research system, it is proved that the addition of sesame seeds concentrate contributes to the growth of MHA indicators. However, with an increase in the replacement of skimmed milk powder with concentrate ("SMP : SSC" ratio of 3.5: 10.0%), an organoleptically unacceptable herbaceous taste appears. In this regard, the rational ratio of "SMP : SSC" revealed by the MHA study is 7.5: 6.0%, which corresponds to the high quality characteristics of the product.

2.6.2 Determination of the influence of recipe components on the moisture state of the research system of the thermostable filling

Moisture type is known to be divided into free and bound by the type of bond. The ratio of free and bound moisture has a very large influence on food production, including TF. After all, knowing the prevailing moisture bond form, it is possible to prevent or correct the changes that the filling undergoes under the influence of certain factors, while maintaining the stability of the TF properties during the action of technological factors (temperature, etc.) [41; 69; 71; 85; 144; 151; 152; 212; 214; 215; 237; 257; 261; 263; 272; 283].

The essence of the NMR method is that due to the creation of a local magnetic field, the water molecule is split into hydrogen and oxygen. In this case, the total molecular mobility of water in the experimental system of thermostable filling is determined by the degree of mobility of hydrogen protons, which determines the time of phase separation of magnetic moments, ie the duration of spin-spin relaxation (T_2) [212]. In Fig. 2.11 shows the duration of spin-spin relaxation of the dipole of water in the TF experimental system under the conditions of the ratio "skimmed milk powder: sesame seed concentrate".

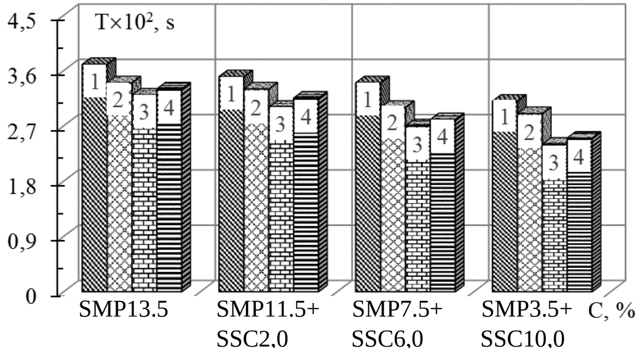


Fig. 2.11 Dependence of the spin-spin relaxation duration of the water dipole in the TF experimental system on the content of SMP and SSC at concentrations: 1 – low-esterified citrus pectin 0,8%; low-esterified citrus pectin and modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%

From fig. 2.11 shows that the duration of spin-spin relaxation (T_2) decreases as the experimental system TN content of hydrocolloids and sesame seed concentrate increases. This indicates the ability of the components of the TF experimental system to absorb and bind moisture with increasing content of hydrocolloids and sesame seeds concentrate.

A similar dependence of the T_2 decrease with the increase in the bound moisture content can be observed provided that the concentration of low-esterified citrus pectin in the TF experimental system is increased to 1.1% with the addition of 1.0% modified corn starch. Thus, during the NMR studies it was found that the duration of spin-spin relaxation of the TF experimental system decreases with increasing concentration of hydrophilic components of protein and polysaccharide nature and ionic polyvalent metals.

To sum up, it can be argued that the rational ratio of skimmed milk powder and sesame seeds concentrate in the experimental system of TF is also 7.5: 6.0%. Due to the increase of concentrate content to 10.0% and, accordingly, reduction of skimmed milk powder to 3.5%, a system with a strong structure and deteriorated organoleptic characteristics is formed.

2.7 Study of influence of recipe components on duration of structure formation and strength of the research system of the thermostable filling

The formulation of the experimental system is combined due to the introduction of animal ingredients (skimmed milk powder) and plant origin ingredients (sesame seed concentrate, low-esterified citrus pectin and modified corn starch). Therefore, in order to form high-quality characteristics of the TF experimental system and taking into account the significant influence of prescription ingredients on the state of moisture in the system, it is necessary to determine the time when the filling will acquire a stable structure, that is, when strong intra- and intermolecular interactions will occur.

The duration of the structure formation of the samples of the TF experimental system under different ratios "SMP: SSC" is shown in Fig. 2.12 and 2.13.

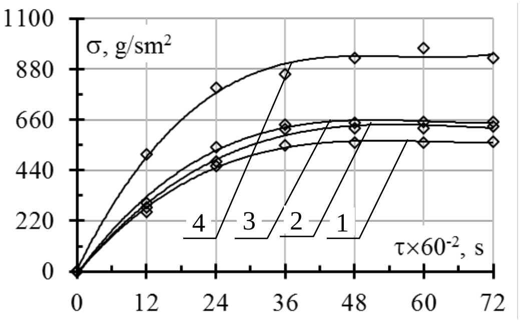
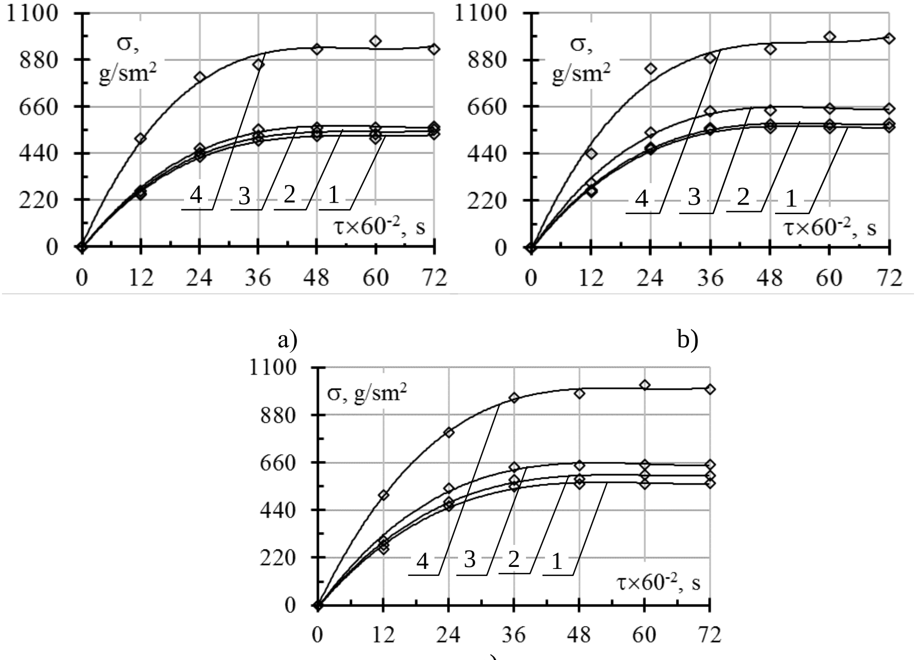


Fig. 2.12. Dependence the strength on the formation time of the TF experimental system with the content of skimmed milk powder 13.5% at concentrations: 1 – low-esterified citrus pectin 0,8%; low-esterified citrus pectinand modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%



a) b)

c)

Fig. 2.13. Dependence the structure formation time on the TF experimental system on the ratio "SPM:SSC": a) 11,5:2,0%; b) 7,5:6,0% i c) 3,5:10,0%,at concentrations: 1 – low-esterified citrus pectin 0,8%; low-esterified citrus pectinand modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%

According to Fig. 2.12 and 2.13, it was found that the addition of sesame seed concentrate to the TF experimental system causes a decrease in the gel strength values. However, there is an increase in the strength of the gel samples of the TF experimental systems relative to each other with an increase in their recipe components, in particular hydrocolloids - low-esterified citrus pectin, modified corn starch and sesame seeds concentrate. It is established that the time of structure formation of combined systems lies in the interval (48…72)×60^2s. It is in this period of time that the strength indicators of the gels of the research systems stabilize, and p to 48×60^2s they increase, which indicates the formation of bonds of different nature between the recipe ingredients. Thus, the formed spatial grid contributes to the emergence of the characteristic structure of the TF experimental system at different concentrations of hydrocolloids and the ratio "SPM:SSC".

In general, the study results of the influence prescription components on the duration of the structure formation of the experimental system thermostable filling revealed that up to 48×60^2s there is a significant increase in the strength of the gel samples. In the interval $(48\ldots72)\times60^2$s, the strength indicators stabilize, the system acquires a stable structure.

Summarizing the obtained results, it is established that according to the strength indicators of suitable for use is the system of TF with a ratio of "SPM:SSC" of 7.5: 6.0% and the content of the mixture of hydrocolloids - low-esterified citrus pectin 0.8% and modified corn starch 3.0 %.

2.8 Investigation of the effective viscosity of thermostable filling

In the technology of thermostable filling production using dairy raw material and sesame seeds concentrate, an important aspect is its viscosity. It determines the fluidity of the filling, that is, the resistance of its movement to the external forces, which characterizes its behavior during the technological operation "pouring into forms". Preliminary studies on the effective viscosity of hydrocolloids and mixtures thereof (low-esterified citrus pectin and modified corn starch) have shown that it is depend on temperature and chemical interactions between components. However, due to the presence in the formulation, in addition to hydrocolloids, components of a protein nature, the fluidity of the finished product is of great importance. Thus, in order to detect the fluidity of the TF experimental system, the dependence of the effective viscosity of the filling at different ratios of "SPM:SSC" on temperature was investigated (Fig. 2.14 and 2.15).

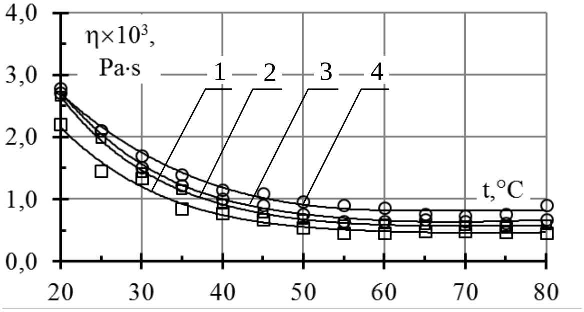
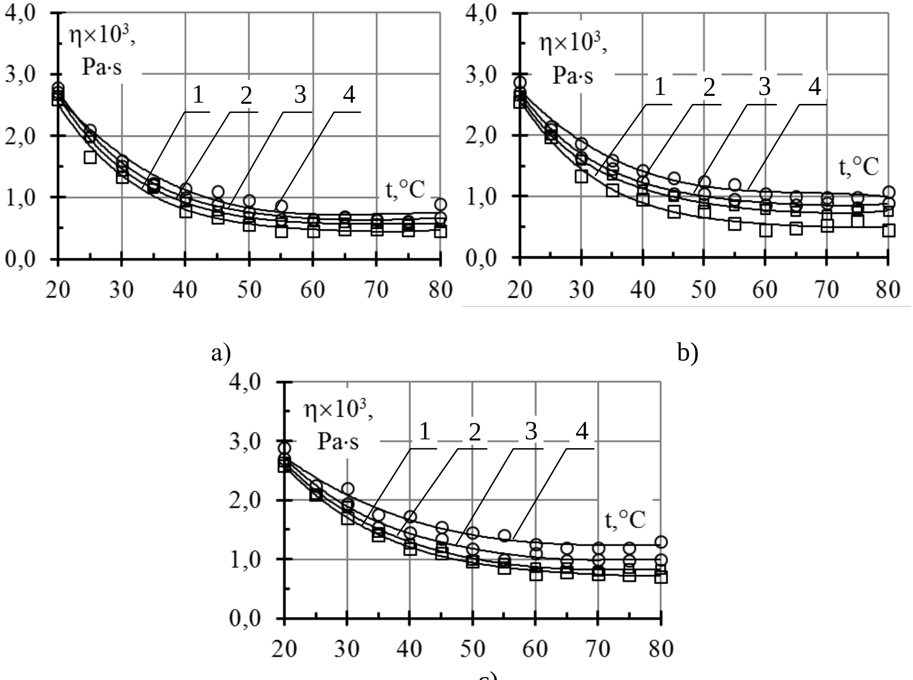


Fig. 2.14. The dependence of the effective viscosity of the TF research system on temperature with a skimmed milk powder content of 13.5% and with concentrations:1 – low-esterified citrus pectin0,8%; low-esterified citrus pectinand modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%



a)

b)

c)

Fig. 2.15. The dependence of the effective viscosity of the TF research system on the temperature at the following ratios "SPM:SSC": a) 11,5:2,0%; b) 7,5:6,0% i c) 3,5:10,0% and at concentrations: 1 – low-esterified citrus pectin 0,8%; low-esterified citrus pectinand modified corn starch respectively: 2 – 0,8% i 1,0%; 3 – 0,8% i 3,0%; 4 – 1,1% i 1,0%

Comparing fig. 2.14 and 2.15, we note the increase in the effective viscosity of systems with partial replacement of skimmed milk powder with sesame seed concentrate. A decrease in the effective viscosity of the TF experimental system was also found, provided that the temperature influence on it was increased. It was found that the values of effective viscosity of the TF experimental system with ratios "SPM:SSC" 11,5: 2,0; 7.5: 6.0 and 3.5%: 10.0% and at different concentrations of hydrocolloids uniformly varies in the temperature range of 60…100°C. Only the TF experimental system at low-esterified citrus pectin concentrations 0,8% and modified corn starch 3,0% with the same ratios "SPM:SSC" has a more intense and almost uniform increase in effective viscosity (approximately from 70°C).In this system, more moisture is bound than at lower starch concentrations. It is established that this system with a ratio of "SPM:SSC" 3.5:10.0% is characterized by a rather high MHA and low molecular mobility (as revealed in the previous experimental studies), requires slightly more force to overcome the resistance, which indicates the formation of a strong structure.

Therefore, the results of studies of effective viscosity confirmed that a rational is TF research system at the concentration of low-esterified citrus pectin 0.8% and modified corn starch 3.0% at a ratio of "SPM:SSC" 7.5:6.0% (by conditions of temperature influence on the system up to 70 °C). By comparing the effective viscosity of the systems with the specified temperature, we prove that this indicator has the lowest values for the concentration of low-esterified citrus pectin 0.8%. Somewhat higher values are in the concentration of low-esterified citrus pectin 0.8 and 1.1% and modified corn starch 1.0%. And the system with a concentration of low-esterified citrus pectin 0.8% and a content of modified corn starch 3.0% has rational values of effective viscosity and is characterized by a plastic consistency within 0.63×10^{-3}Pa·s.

2.9 Investigation of IR spectroscopic parameters of the research system of the thermostable filling

Due to the combination and introduction of established concentrations of protein-polysaccharide components (skimmed milk powder, sesame seed concentrate, low-esterified citrus pectin and modified corn starch), the filling acquires thermostable properties. The IR spectroscopy method was used to confirm these necessary positive effects and to identify the linkages between the formulation components of the TF research system.

It is known that the radiation of the IR spectra depends on the general structure of the molecule and its environment, the group of atoms that make up it, and the individual bonds between them (electron polarization). The molecule can only be in certain energy relations. Each energy level corresponds to its total energy, which characterizes the transition of a molecule from one level to another. At the same time, only the radiation frequency is absorbed, the energy of which is equal to the energy difference of any two levels, that is, those wavelengths can be absorbed that can change their energy state.The release of energy that causes oscillations of atoms in a molecule is accompanied by absorption of the IR spectra by changing the dipole moment of the molecule [204; 242; 244; 251; 252]. The effect of infrared radiation with a constant variable frequency on the research system causes to absorb by molecule certain radiation links, which cause deformation of the corresponding bonds (Table 2.6), which are recorded as bands with a minimum and maximum oscillation frequency (Fig. 2.16).

Table 2.6

Characteristic bands of the valence vibrations of the TF experimental system

Sample number	Peaks area, cm^{-1}	Assignment of bands	Conclusion
1	2	3	4
1 – 8	3600…3100	Valence vibrations of the group OH	Characterized by the construction of intermolecular hydrogen bonds
4 – 8	3350…2850	Valence vibrations of the group CH	Characterized by the structure of alkanes
4 – 8	2440…2350	Valence vibrations of the groupC≡C	Characterized by the structure of alkenes

Continuation of Table 2.6

1	2	3	4
1 – 8	2140…2100	Fluctuations of organophosphorus groups P-H	Conditioned by the construction of connections with a presence of dairy base
1 – 6	1680…1620	Vibrations of the group C=C	Characterized by the structure of alkenes
1 – 6	1470…1355	Symmetrically deformational vibrations of the group CH_3	Characterized by the structure of alkanes
1 – 6	1350…1280	Valence vibrations of the group C-N	Characterizes peptide bonds
1 – 6	1280…1150	Fluctuations of the ether groupC-O-C	Characterized by the structure of the ethereal bonds
1 – 8	1100…900	Valence vibrations of the group CH	Characterized by the structure of alkanes
1, 3 –5, 7	550…450	Vibrations of the groupS=S	Characterized by the structure of proteins

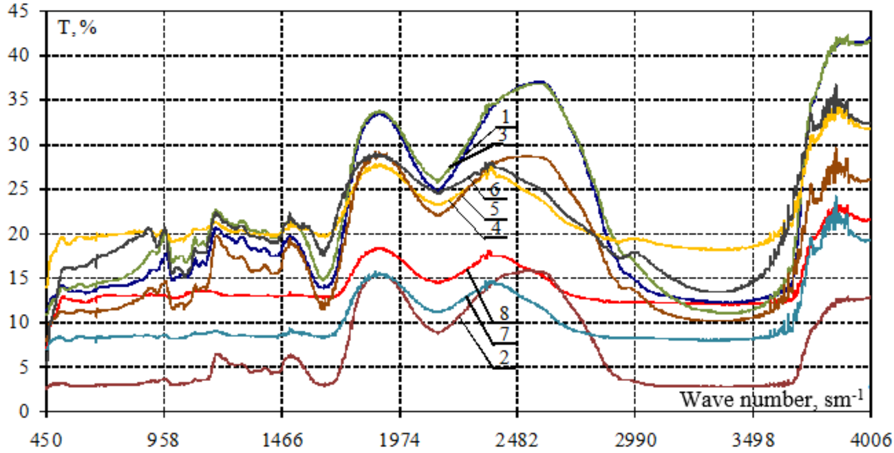


Fig. 2.16. IR spectra of samples of TF experimental systems:
1 – concentration of low-esterified citrus pectin 0,8%;
2 – ratio "pectin:starch"0,8:3,0%;
3 – ratio "pectin:calcium citrate"0,8:0,04%;
4 – ratio "pectin:skimmed milk powder"0,8:7,5%;
5 – ratio "pectin:starch:calcium citrate"0,8:3,0:0,04%;
6 – ratio "pectin:skimmed milk powder:calcium citrate" 0,8:7,5:0,04%;
7 – ratio "pectin:starch:skimmed milk powder" 0,8:3,0:7,5%;
8 – ratio «pectin:starch:skimmed milk powder:calcium citrate» 0,8:3,0:7,5:0,04%

From the above Fig. 2.16 shows that during the step-by-step introduction into the experimental system of thermostable filling with a concentration of low-esterified citrus pectin of 0.8% and recipe components (modified corn starch, sesame seed concentrate, skimmed milk powder and calcium citrate) identical strips of absorption in the range of wave lengths 3600…3100см$^{-1}$, 2140…2100см$^{-1}$and 1100…900см$^{-1}$ are observed, which characterizes the valence vibrations of the OH, C≡C and CH groups. OH - groups are involved in the construction of intermolecular hydrogen bonds, C≡C characterize the structure of alkenes and CH - alkanes.The absorption spectrum at ν = 3350… 2850 cm^{-1}characterizes alkane compounds, and the bands in the range 2440… 2100 characterize the organophosphorus P-H bonds that are available for the TF experimental systems (4–8) with the content of skimmed milk powder and calcium citrate which are the source of polyvalent metals, namely Ca^{2+} ions. They crosslink pectin molecules through the formation of calcium bridges.

Based on the above results, we trace the tendency for the absorption of the corresponding groups: OH, CH, PH, C≡C, CH and S=S, indicating the occurrence of molecular and intermolecular interactions between the prescription components. Thus, the influence of each formulation component on the experimental system is determined by detecting interactions with their sequential introduction.

Thus, during the researches the occurrence of physicochemical interactions between the prescription components of the experimental system of TF, which contribute to the formation of fillings with stable physicochemical parameters and high structural-mechanical and thermostable properties, was established.

2.10 Establishing a rational ratio of the recipe components of the research system of the thermostable filling and the principles of recipe development

The main recipe components of the protein-polysaccharide nature, which are part of TF composition (skimmed milk powder, sesame seed concentrate, low-esterified citrus pectin, starch and calcium citrate), play a significant role in the formation of its organoleptic characteristics and other properties (physical-chemical, structural, mechanical and technological). In the Table 2.7. the organoleptic characteristics of the TF experimental system with different ratios of prescription components are presented.

Table2.7

Organoleptic characteristics of the TF experimental system

Prescription components	Contents, %	Appearance, consistency	Color	Taste and smell
"pectin:skimmed milk powder"	0,8:1,5	Very weak gel, low density	From white with a grayish tint to light yellow	Pleasant, slightly dairy aroma. With a pure, sweet, slightly dairy (or milky) taste. No extraneous smacks (or with a slight sandiness)
	0,8:5,5			
	0,8:9,5	Very weak gel, slightly dense		
	0,8:13,5	Weak, dense gel		
	0,8:17,5			
"pectin:starch: skimmed milk powder"	0,8:1,0:1,5	From smear to gentle, in measure of low density	From pale white to light yellow	Pleasant, slightly dairy aroma. With a pure, sweet, viscous (gentle) slightly dairy (or milky) taste.No extraneous smacks (or with a slight sandiness)
	0,8:1,0:5,5			
	0,8:1,0:9,5			
	0,8:1,0:13,5			
	0,8:1,0:17,5			
	0,8:3,0:1,5	From smear, plastic, gentle to soft, gel-like, dense consistency		
	0,8:3,0:5,5			
	0,8:3,0:9,5			
	0,8:3,0:13,5			
	0,8:3,0:17,5			
"pectin: sesame seeds concentrate: skimmed milk powder"	0,8:2,0:11,5	From gentle, flexible, soft, smooth to slightly dense consistency	From grayish to light yellow	Pleasant, slightly dairy aroma. With a pure, sweet, slightly dairy and slightly sesame (milky or herbaceous) taste
	0,8:6,0:7,5			
	0,8:10,0:3,5			
"pectin: sesame seeds concentrate: skimmed milk powder"	0,8:1,0:2,0:11,5	The consistency is elastic, in measure of dense, low strength	From grayish to light yellow	Pleasant, slightly dairy aroma. With pure, sweet, slightly dairy and in measure sesame (dairy or herbaceous) taste
	0,8:1,0:6,0:7,5			
	0,8:1,0:10,0:3,5	From soft, plastic, homogeneous consistency throughout the mass to dense		
	0,8:3,0:2,0:11,5			
	0,8:3,0:6,0:7,5	From plastic, soft, gentle, elastic, gel-like uniform throughout the mass to a dense consistency		
	0,8:3,0:10,0:3,5			
	1,1:1,0:2,0:11,5	Strong, slightly plastic, elastic, too dense consistency		
	1,1:1,0:6,0:7,5			
	1,1:1,0:10,0:3,5			

According to the above organoleptic characteristics of the TF experimental system, it was found that the softest, gel-like and dense consistency is characteristic of the system with the content of low-esterified citrus pectin 0.8%, modified corn starch 3.0% and skimmed milk powder 13.5%. The same is true for the skimmed milk powder content of 7.5% and the sesame seed concentrate of 6.0%. An TF experimental system with increasing the content of these prescription components acquires a strong, too dense consistency with a more saturated milky and sesame (herbaceous) taste.

It has been discovered that during the production of the filling, the raw material undergoes changes at the physicochemical level: there arise links between the animal (dairy component), plant and fat components, which leads to their rearrangement and formation of calcium bridges.

The production of thermostable filling using dairy raw materials and sesame seeds concentrate begins with the preparation of dry components to obtain a milk base (D_1) and a pectin-sugar mixture (D_2). The milk base is obtained by sequential mixing of the milk-starch mixture and the emulsion system.

The milk-starch mixture is formed as a result of the interaction of recovered milk, which has been pre-heat-treated, that is, restored at temperatures of 30…35°C for $(1…3)\times60^2$ s and pasteurized at 70…74°C for 20…25 s, followed by the introduction of modified corn starch and concentrate of sesame seeds obtained by cold pressing, which causes the preservation of all nutrients.

While sustain skimmed milk powder, the particles are moistened and increased in volume. There arise a close interaction between the constituent parts, which causes their transition into solution: lactose - from the amorphous state to crystalline, the protein - into colloidal (particle size from 15 to 30 nm) and others, which are in the ion-molecular state (size about 1 nm and less).

Upon completion of the restoration, a complex polydisperse system is pasteurized and further cooled for the introduction of starch and sesame seed concentrate to neutralize extraneous microflora and inactivate the lipase enzyme. Starch swells. In the starch grain, due to the weakening and destruction of some hydrogen bonds during the heat treatment, creates a void where water enters. This leads to an increase in starch grain volume and the emergence of new hydrogen bonds [57; 248; 276; 293]. Sesame seed concentrate, which has a high protein content (about 45%) and low fat (about 8%), during the interaction with the solvent is characterized by swelling of protein molecules. Its particle size is from 50 to 150 microns, which is organoleptically not felt, thus indicating high moisture and fat-holding properties [4]. Formed in this way, hydrophilic centers, through interactions of different nature, are combined with other components of the system with the formation of a milk-starch mixture characterized by a complex polydispersed medium with a viscous consistency.

The emulsion system is formed as a result of the addition of refined deodorized sunflower oil at a temperature of 32…36°C with emulsification for (2…3)×60 s into the milk-starch mixture.

It is known that the presence of fat in the composition of powdered milk worsens its swelling, the transition of protein into solution and the dispersion of fat [37], so to obtain reconstituted milk with the physico-chemical properties of natural, the oil is introduced after completion of swelling. During the emulsification of fatty milk components, there is a redistribution between the constituent particles, which are transformed into fatty protein complexes.

The main structural element of the protein is casein micelles, consisting of sub-micelles with a diameter of 10-15 nm, and they, in turn - from the subunits of the basic fractions of casein (αs_1, αs_2, $\beta i \chi$), interconnected by hydrophobic, electrostatic, hydrogen bonds and calcium bridges [252; 260; 299 - 302]. The polypeptide chains of the casein fractions are folded in such a way in sub-micelles that its inner part form hydrophobic bonds, and in the outer part are hydrophilic ones, represented by the negatively charged acid groups.

Due to hydrophobic bonds around the fat molecule is distributed protein shell, which is connected by hydrophilic bonds with starch and aqueous medium, that is, due to the orientation of hydrophobic and hydrophilic sections of the protein, their ability to adsorb on the surface of phase distribution with the formation of a related medium is demonstrated. [250; 273; 300; 302]

Obtaining a pectin-sugar mixture (D2) consists of mixing sugar with pectin, adding water at a temperature of 40…45°C, stirring for 1×60^2 s and further swelling within $(20…24)\times60^2$ s. To prevent the formation of lumps, uniform and homogeneous distribution of pectin particles in the mixture, it is pre-mixed with sugar and introduced into water. The pectin molecule has a spiral shape [236; 261; 263; 268; 279]. In the case of their convergence, voids arise, where form carboxylic and hydroxyl groups, which cause to form hydrogen bonds as a result of the interaction with the sugar oxy groups [242; 249; 268; 273; 279; 281; 285; 293].

The next step is subsystem C - mixing and heat treatment, characterized by the connection of the milk base (D_1) and the pectin-sugar mixture (D_2). By interacting with water, pectin molecules dissociate with the formation of COO– ions, causing the molecules to acquire a negative charge and there is a repulsive force between them, which is suppressed by the addition of divalent metal ions (Ca^{2+}), i.e. by the addition of a milk base [242; 250; 253; 261; 287]. Due to heat treatment, starch grains absorb a large amount of water, increase in volume and form a starch paste, which is intertwined with the pectin chain to form a three-dimensional spatial grid. The formation of the gel occurs in several stages: with a small content of calcium ions, the pectin molecules approach and orient due to joining the carboxylic groups of two adjacent pectin molecules by calcium ions [242; 250; 268; 273; 279; 285; 294; 296].

Subsystem B - casting and structure formation. At this stage, the structural and mechanical properties of the product are formed due to the introduction of calcium citrate for $(48…72)\times60^2$ s. Increasing the concentration of calcium ions in the system promotes the formation of complexes with calcium. Intermolecular interactions and the formation of calcium bridges occur, which crosslink pectin molecules, interact with their carboxyl groups, and form a spatial network that binds all the constituent components of the TF system together [94; 148; 242; 250; 256; 273; 281;292; 293; 302].

The last stage is subsystem A - obtaining thermostable filling with the use of dairy raw material and sesame seeds concentrate - characterized by obtaining a structured product with certain physical, chemical and structural-mechanical properties. Its shelf life under normal storage conditions (0…4°C) is 15 days. In order to prolong the shelf life up to 6 months, rapid freezing at –18±2 °C was used, which facilitates the formation of a large number of crystallization centers [25; 94; 148; 281]. Thus, small crystals of ice arise, which preserve the textural, physicochemical and biochemical properties of the filling at the molecular level.

3 Development of technology of thermostable fillings with using dairy raw materials and sesame seeds concentrate and study of its quality indicators under traditional storage conditions and frozen

3.1Development of recipe and technology of thermostable filling using dairy raw material and sesame seeds concentrate

The use of various heat-resistant fillings is the source of an assortment of gingerbread, various types of cookies, muffins, rolls and other flour confectionery products. Common products (jam, marmalade, confiture) during heat treatment boil, float, burn, and are absorbed into the dough [15]. Thermostable fillings do not have these disadvantages. They retain their properties under normal baking conditions.

Thermostable fillings are a typical semi-finished product that confectionery companies usually receive ready-made. It is possible make them directly in the confectionery industry, for which it is necessery to mix the usual filling with a heat-resistant additive (pectin or a mixture of hydrocolloids).

The melting point of the heat-resistant filling is above 200°C.

The melting temperature of the filling with limited thermostable properties is in the range from 115°C to 200°C with a similar temperature distribution during temperature exposure.

The melting point of a non-thermostable filling is below 115°C. When baking at 200°C, non-thermostable fillings melt and completely change their shape, the shape of a filling with limited heat-resistant properties is preserved, the surface is slightly touched up and becomes glossy, heat-resistant fillings do not change their shape and their surface remains matte.

It is useful for a confectioner to know the methods of evaluating a heat-resistant filling in order to predict the results of its use. They are based on the principle of modeling the temperature effect, as well as its duration on the studied product under certain conditions (filling shape, temperature effect on the product). Three methods for controlling heat-resistant properties are offered:

- method of low (M1) temperature exposure;

- method of average (M2) temperature exposure;
- method of high (M3) temperature exposure.

For control by the M1 method, the filling is applied through a template to the dough, then baked in a preheated oven at 200°C for 15×60 s. The shape of the filling should not change.

For control by the M2 method, the filling is applied to the dough through a metal ring, which gives it a standard shape. Then bake in an oven at 200°C for 20x60 seconds.

For control by the M3 method, the filling is applied through a metal ring to filter paper and baked at 200°C for 20 minutes.

As an additional criterion, it is proposed to use the ability of fillings to syneresis, which negatively affects the quality of confectionery products after baking. This study is carried out by keeping less than 30x60 s on filter paper at room temperature. The formation on the paper around the filling of the "absorption zone" of a characteristic color indicates the separation of moisture. The larger the area of the "zone", the higher the tendency of the filling to syneresis and the worse its heat-resistant properties.

In the production of fillings with a certain melting point, there is a general rule: the higher the gelation temperature of pectin, the higher the melting point of the filling will be. However, this rule limits the use of highly esterified pectins in the recipes of heat-resistant fillings, as they form a very strong structure at a sufficiently high gelation temperature.

At the same time, the heat-resistant properties of such gels completely depend on the integrity of their structure, that is, the destruction of the structure during mechanical action (for example, pumping) leads to a complete loss of heat resistance. In this case, the filling on highly esterified pectin boils, deforms and flows out of the product. Therefore, milk fillings based on highly esterified pectins with such properties can be used only at enterprises with a small volume of production and manual dosing of the filling into (on) the product, in which its structure is preserved.

Only in such conditions can the structure of the filling and its heat-resistant properties be preserved [7].

For large enterprises, the use of special low-esterified pectins in the recipes of heat-resistant fillings is envisaged. The consistency of the latter must be preserved or reversible, that is, restored after destruction in conditions of a high level of mechanization and continuous production, in which there is a repeated violation of the structure (for example, during pumping), accompanied in some cases by heating or cooling of the filling. The properties of low-esterified pectins contribute to the formation of the necessary consistency and structure of the filling.

As you know, low-esterified pectins, like high-esterified ones, form a gel in the presence of a sufficient amount of dissolved solids and acid. However, unlike high-esterified pectins, low-esterified pectins are able to form gels when interacting with polyvalent metal ions, for example with calcium, regardless of the pH value and the content of dry substances in the product. The formation of the filling with the participation of low-esterified pectins and calcium ions takes place in several stages: with a small content of calcium ions, the convergence and orientation of pectin molecules occurs: • at a given concentration of calcium, calcium bridges are formed;

• with an overdose of calcium, in otherwise unchanged conditions of preparation of the filling, precipitation of calcium pectin occurs, usually this stage is designated as "premature" gelling.

Special attention is paid to the preparation of the calcium citrate suspension when making the filling. It should be completely homogeneous, without large lumps of calcium citrate. The introduction of properly prepared calcium citrate suspension into the recipe mixture at the last stage of cooking should take place at a temperature below 80°C and be accompanied by intensive mixing. Such technological operations help to prevent the so-called "local" structure formation in the volume of the prescription mass.

With premature gelation, the structure of the filling becomes less elastic. It acquires pasty properties and low internal strength.

The process of gelation of pectins is a reaction that largely depends on temperature. To fully characterize the process, it is necessary to accurately determine the temperature at which the formation of a certain structure occurs after the end of cooking. At this temperature, the transition of the liquid recipe mass to the specified state occurs. At this stage, pectin molecules are oriented and a three-dimensional spatial structure is formed, in which water and sugar are in a bound state. Mechanical interaction, for example, pumping and (or) mixing at a temperature that decreases, interferes with the spatial orientation of molecules and destroys already formed associations of pectin chains. In this case, it is impossible to form a strong and homogeneous definite structure. After the completion of the mechanical interaction at temperatures significantly below the gelation temperature, a new reorientation of pectin molecules occurs, therefore, the formation of a strong structure is practically impossible. For this, it is necessary to reheat the system to a temperature above the gelation temperature. The gelation temperature of fillings based on low-esterified pectins depends on the dosage of calcium. Increased dosage of calcium leads to intense convergence of pectin molecules even at high temperatures (above 80°C). Thus, if all other parameters of the product are maintained at a constant level, gelation increases with a simultaneous increase in calcium dosage.

Mechanical interaction during gelation always occurs when the filling is poured. If the pouring takes place at a temperature below the gelation temperature, then the formation of a pasty structure occurs due to the effect of premature gelation.

Heat-resistant filling is a product with a certain structure, made on the basis of dry milk, special structure-forming and jelly components, consistency stabilizers and other ingredients, which are used in the production of bakery or flour confectionery products and retain their organoleptic, physical and chemical properties (form, volume, texture, dry matter content, active acidity, etc.) under normal baking conditions (convection method, temperature 210 ... 230°C, duration 10...20x60 sec). Ready heat-resistant milk filling should have the following properties:

- color characteristic of the raw materials used;
- high viscosity;

- pronounced aroma and taste of the raw materials used;
- good mixing ability;
- resistance to mechanical interaction, for example, storage of the structure during pumping;
- sufficient strength and stability after giving the filling a certain shape during mechanical or manual dosing;
- lack of liquidity;
- absence of syneresis (release of moisture and separation of phases) during storage of the filling or during mechanical action;
- a partial loss of elasticity (viscosity) is allowed when it is slowly heated to a temperature close to 60°C in order to improve pumping ability.

The structure that characterizes the structure of the filling, as well as its composition and homogeneity, must have the following properties:

- high degree of homogeneity;
- absence of jelly lumps or clots (result of incorrect management of the technological process and a sign of local gelation of the recipe mass in the boiler after adding calcium citrate suspension);
- absence of components uncharacteristic for the use of dairy raw materials;
- characteristic shiny outer surface, indicating good gelation;
- characteristic detachment from the inner wall of the container (clearly visible when pouring into a glass container);
- a characteristic short structure (when dosing in (on) culinary and confectionery products through the dosing machine, there should be no so-called "tails" and hanging of the filling from the dosing element);
- the presence of small particles of used milk raw materials in the filling is allowed, which should not interfere with the pumping of the filling.

Heat-resistant fillings, as well as fillings with increased heat resistance, are used for simultaneous baking with confectionery products [25].

While developing the technology of milk fillings based on low-esterified petin with the addition of starch, the following technological steps were performed:

- substantiated the method of introducing starch and calcium citrate into product formulations;
- the amount of pectin reduction and starch addition was determined;
- derived the optimal technological parameters that allow obtaining the required amount of reducing substances [26].

In previous studies, it was found that the main recipe components that give thermostable and structural-mechanical properties of TF are hydrocolloids - modified corn starch and low-esterified citrus pectin. These hydrocolloids, together with calcium ions (contained in dairy raw materials and calcium citrate), which "crosslink" pectin molecules to form calcium bridges, are constituent units of a strong spatial grid of filling. It was also found that the addition of sesame seeds concentrate to the filling, has a positive effect on a number of physico-chemical parameters of the product.Thus, the results of the research of analytical, organoleptic, structural-mechanical, a number of physicochemical and technological properties of the experimental system of thermostable filling became the reason for further scientific substantiation of the formulation (Tables 3.1 and 3.2) and technology of production of thermostable filling (Fig. 3.1).

In order to clearly demonstrate the positive effect of sesame seeds concentrate on the quality characteristics of the filling, the results of the experimental studies are further presented in the section with a comparison of the results obtained from studies of the control sample of thermostable filling made without adding the sesame seed concentrate according to the recipe in Table 3.1, and a sample of thermostable filling using dairy raw materials and sesame seeds concentrate (recipe is provided in Table 3.2).

Table 3.1

Consolidated recipe of thermostable filling per 100 kg

№	Raw materials	Mass fraction of solids, %	Calculation rate per 100 kg filling, kg	
			In reality	In solids
1.	White sugar	99,85	35,99	35,94
2.	Skimmed milk powder	96,00	14,19	13,63
3.	Starch treacle	78,00	5,07	3,65
4.	Modified corn starch	88,00	3,04	2,68
5.	Refined deodorized sunflower oil	99,90	2,53	2,53
6.	Low-esterified citrus pectin	90,00	0,81	0,73
7.	Calcium citrate	97,00	0,04	0,04
8.	Drinking water	–	41,4	–
Total		-	105,30	59,20
Product yield		56,22	100,00	56,22

Table 3.2

Consolidated recipe of thermostable filling using dairy raw material and sesame seeds concentrate per 100 kg

№	Raw materials	Mass fraction of solids, %	Calculation rate per 100 kg filling, kg	
			In reality	In solids
1.	White sugar	99,85	36,00	35,99
2.	Skimmed milk powder	96,00	7,90	7,59
3.	Sesame seed concentrate	92,00	6,30	5,80
4.	Starch treacle	78,00	5,00	3,60
5.	Modified corn starch	88,00	3,00	2,64
6.	Low-esterified citrus pectin	90,00	0,80	0,72
7.	Refined deodorized sunflower oil	99,90	2,10	2,10
8.	Calcium citrate	97,00	0,04	0,04
9.	Drinking water	–	44,30	–
Total		–	105,30	58,48
Product yield		55,54	100,00	55,54

The technological system of the TF production consists of four logically and functionally interconnected subsystems. In the first stage - preparation of prescription components (subsystem D) is mixed low-esterified pectin citrus with ⅛ a part of sugar and ⅓ a part of drinking water at a temperature of 40…45°C, carefully mixed and stayed for swelling at (20…24)×60^2 s. The skimmed milk powder is mixed with drinking water at temperatures of 30…35°C and sustained for (1…3)×60^2 s. The reconstituted milk is pasteurized at 70…74°C for 15…20s, cooled to 32…36°C, added modified corn starch and remaining sugar. For receiving thermostable filling of milk-plant composition with these components is entered a pre-prepared sesame seed concentrate. Further mix is mixed for (10…15 ×60 s. After that is added the refined deodorized sunflower oil and emulsify at a rotating speed of 25±1 s^{-1} at 32…36°C for (2…3)×60 s.

The second stage is mixing and heat treatment (subsystem C). The prepared pectin mixture is boiled at temperatures in the range of 55…85°C to a solids content of 25±1.5%, the obtained combined base is added and continue to boil to a mass fraction of solids 46±1.5%, then added the starch treacle and boil to the contents solids 56.5±1.5%. At (2…3)×60 s before the end of the boiling process, a pre-prepared 1% solution of calcium citrate is introduced. A solution of calcium citrate is prepared with the addition of citric acid.

The third stage is spilling and structure formation (subsystem B). The resulting system is stirred and poured into a container for structure formation that occurs within 60±12×60^2 s. The resulting product is then packed.

The fourth stage is to obtain thermostable filling with the use of dairy raw materials and sesame seeds concentrate (subsystem A). Ready TF, regardless of the presence in its composition of sesame seeds concentrate, has the following organoleptic characteristics: appearance and consistency - homogeneous, gentle, in measure of dense; filling color - from white to light yellow; smell - inherent in prescription components; the taste is sweet, inherent in the recipe components used. Storage and realization of TH is carried out in three directions.The first direction is the direct realization of the TF within 36 hours after packing at a temperature of 12±2 °C and a relative humidity of 75±2%. The second direction involves the storage of TF for 15 days at a temperature of 0 ... 4°C and a relative humidity of 75±2%. Third direction - freezing - storage of TF at temperatures -18±2°C for no more than 4 months with a relative humidity of 94±2%. Thus, the connection sequence of the subsystems has a defined purpose and function (Table 3.3).

Table 3.3

Structure of technological system of TF production

Name of subsystem (stage)	Name of the subsystemand operations	Characteristics functioning of subsystems (stage)
D «Preparation of prescription components»	D_1 «Obtaining a combined basis»: – mixing; – restorationandmixing; – pasteurization; – cooling; – mixing; – emulsification	Quantity and quality control. Ensuring dissolution and swelling.
	D_2 «Obtaining a pectin-sugar mixture»: – siftings; – compound; – mixing; – swelling; – filtering	
C «Mixing and heat treatment»	Heat treatment (boiling)	Compound of prescription components, formation of structural-mechanical and physicochemical properties
	Filtering	
B «Spilling and structure formation»	Spill into molds	Providing the form, structure and necessary qualitative characteristics of TF
	Structure formation	
	Packing	
A «Obtain thermostable filling with the use of dairy raw materials and sesame seeds concentrate»	A_1 «Realization»: – realization	Obtaining TF with specified organoleptic, physicochemical, structural-mechanical and microbiological characteristics (with the possibility of storage in the frozen state)
	A_2 «Short-term storage»: – storage	
	A_3 «Long-term storage»: – freezing; – storage	

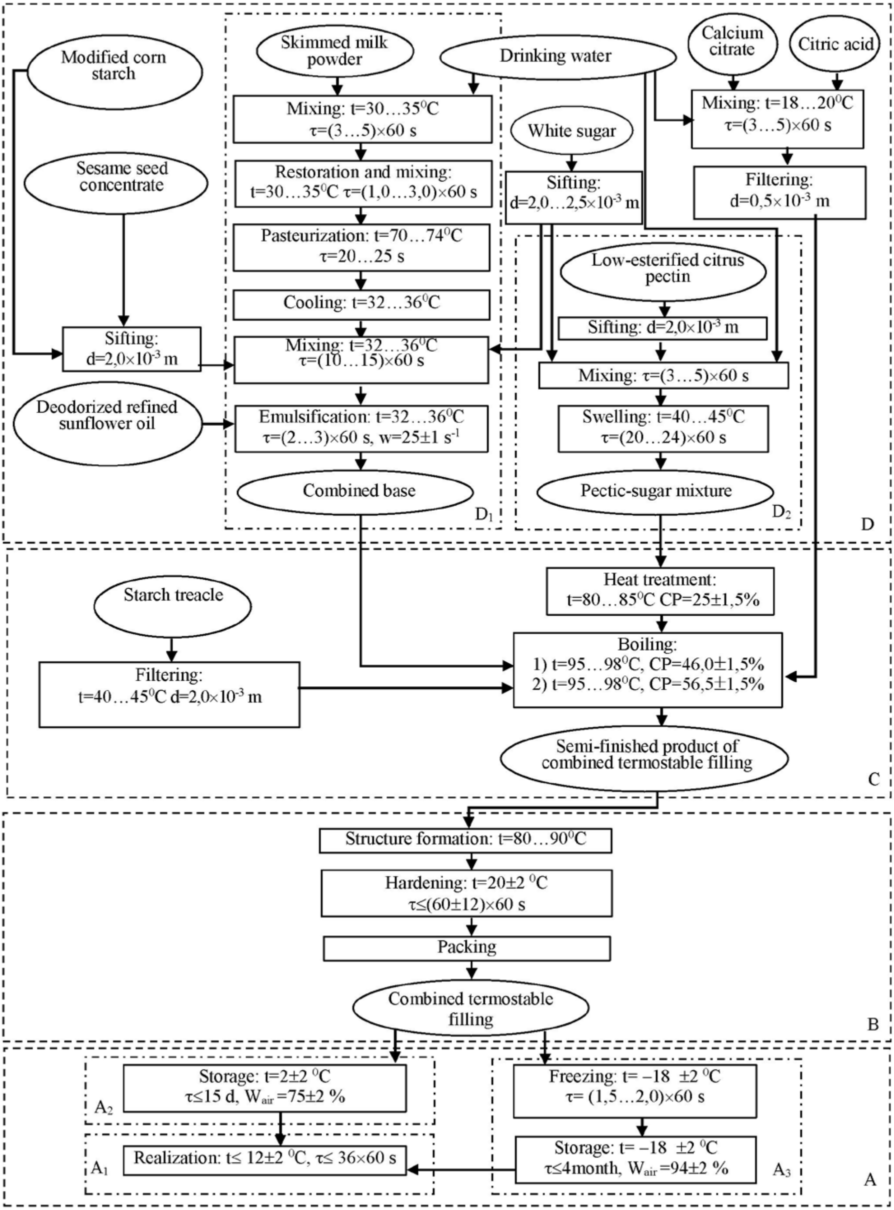


Fig. 3.1. Technological scheme of thermostable frozen filling using dairy raw materials and sesame seeds concentrate

3.2 Study of microbiological indicators of thermostable filling using dairy raw material and sesame seeds concentrate and justification of its storage life under traditional conditions and frozen

Microbiological indicators are important fundamental indicators of the quality of thermostable fillings, which determine their suitability for consumption. Given that the developed TF contains about 45% moisture, it is a receptive medium for the development of microorganisms. Due to the attraction to the TF formulation the components of protein-polysaccharide nature with high hydrophilic properties and moisture retention, some moisture becomes bound. However, there is a risk of introducing harmful microflora: molds and yeast, so there is a need to study the microbiological parameters of TF (Table 3.4).

Table 3.4

Microbiological indicators of TF

Indicator	TF control sample					Developed TF sample with sesame seed concentrate				
	Freshly made	Storage temperature, °C				Freshly made	Storage temperature, °C			
		2±2		−18±2			2±2		−18±2	
		after 15 days	after 28 days	after 4 months	after 6 months		after 15 days	after 28 days	after 4 months	after 6 months
Quantity of Mesophilic Aerobic and Facultative Anaerobic Microorganisms (QMAFAM), number of conventional units(NCU) in 1 g not more $1,0\times10^3$	$0,5\times10^3$	$0,7\times10^3$	$1,0\times10^3$	$0,9\times10^3$	$1,0\times10^3$	$0,5\times10^3$	$0,75\times10^3$	$1,0\times10^3$	$0,85\times10^3$	$1,0\times10^3$
E. coli bacteria, in0.001 g is not allowed	Not detected					Not detected				
Conditionally pathogenic microorganisms, including Staphylococcus aureus,in 0.1 g is not allowedNCU	Not detected					Not detected				
Pathogenic microorganisms, including Salmonella, in 25 g is not allowed	Not detected					Not detected				
Amount of yeast and mold,in 1 g not more50 NCU	Not detected					Not detected				

It can be seen from Table 3.4 shows that the microbiological parameters of the samples of TF - freshly made and the samples stored at 2±2 °C for 15 days - do not exceed the norms [106]. The final norm of QMAFAM $1,0 \times 10^3$ NCU in 1 g reaches the samples after 28 days of storage at the same temperature and after 6 months of storage at a temperature of -18±2°C. Therefore, it is advisable to use low temperatures to prevent unwanted changes and preserve the quality characteristics of development.

Thus, according to the results of TF microbiological studies, the recommended shelf life at 2±2 °C is 15 days, and at temperatures of –18±2 °C - 4 months. Taking into account this results, it is advisable to submit the results of further experimental studies under the established rational storage conditions, under which the proposed thermostable fillings meets the microbiological norms of the current medical and biological requirements and sanitary quality standards [106].

3.3 Study of the chemical composition of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

The thermostable filling is a complex system consisting of a certain number of components of a particular nutritional and biological value. During the development of the TF formulation composition it was guided by the promising direction of creating a combined product of high biological value with specified thermostable, structural, mechanical and physico-chemical characteristics. This was achieved by the joint use of hydrocolloids of different nature and the introduction into the TF formulation of protein plant product - sesame seed concentrate [123; 159]. That is why, in order to understand the biological and nutritional value of TF, it is necessary to present a series of studies on the chemical composition of scientific development. General characteristics of the TF chemical composition are given in Table 3.5.

Table 3.5

Characterization of the TF chemical composition

Name of component	Contents, %					
	TF control sample			Developed TF sample with sesame seed concentrate		
	Freshly made	Storage temperature, °C		Freshly made	Storage temperature, °C	
		2 ± 2 after 15 days	–18 ± 2 after 4 months		2 ± 2 after 15 days	–18 ± 2 after 4 months
Proteins	5,00±0,25	5,00±0,25	5,08±0,25	5,10±0,26	5,10±0,26	5,16±0,26
Fats	2,53±0,13	2,55±0,13	2,62±0,13	2,48±0,10	2,50±0,10	2,58±0,10
Carbohydrates	45,63±2,30	45,63±2,30	45,63±2,30	41,35±2,10	41,35±2,10	41,35±2,10
Dietary fiber	0,95±0,03	0,95±0,03	0,95±0,03	0,95±0,03	0,95±0,03	0,95±0,03
Moisture	42,30±2,00	41,40±2,00	40,00±2,00	45,30±2,20	44,30±2,20	42,00±2,10

From the data Table 3.5 shows that the nutrients of both freshly made samples of TF remain at almost the same level after storage under traditional conditions for 15 days (slightly reduced moisture). The total amount of proteins, fats and carbohydrates at a storage temperature of 2±2°C of the TF control sample is 5.00, 2.55 and 45.63%, respectively, and the developed TF sample with the addition of sesame seeds concentrate, respectively 5.10, 2.50 and 41.35%. It was found that the total number of dietary fiber under different regimes and the duration of storage of these samples remains unchanged - 0.95%.

Experimental studies have shown that a number of physico-chemical and biochemical processes undergo the filling of changes during storage. In particular, during freezing due to moisture crystallization, it is possible to damage protein and polysaccharide molecules by large ice crystals, accompanied by moisture loss. This is confirmed by the results of the moisture change (Table 3.5): according to the results of the chemical composition evaluation of the developed samples at a storage temperature of -18±2°C, the total amount of proteins and fats increases, and moisture - decreases relative to the samples stored at a temperature of 2±2°C 15 days.Therefore, due to the loss of moisture by the control and developed samples of TF with a plant protein supplement (respectively 3.4 and 5.2%) after their defrosting, the amount of protein substances is concentrated, which is accompanied by an increase of proteins by 1.6 and 1.2%, respectively. The total fat content in these samples increases respectively by 2.7 and 3.2%. It is likely that the increase in fat content after defrosting is due to oxidation and hydrolysis processes [31; 129; 131; 147]. Thus, freezing contributes to a slight loss of moisture with a parallel increase (concentration) of nutrients.

Since a certain amount of protein in the developed filling is caused by the use of plant protein-containing raw material - sesame seed concentrate, it is necessary to provide a comparative characteristic of the amino acid content of the sesame seeds and directly in its concentrate (Table 3.6).

Table 3.6

Comparative characteristics of the amino acid composition of the raw material

The name of the component	Contents, %	
	Sesame seeds	Sesame seed concentrate
Water	9,00	8,00
Protein	19,40	45,00
Essential amino acids		
Valine	1,20±0,06	2,78±0,1
Isoleucine	0,90±0,05	2,09±0,10
Leucine	1,60±0,08	3,71±0,20
Lysine	0,67±0,03	1,55±0,08
Methionine	0,70±0,04	1,62±0,08
Threonine	0,87±0,04	2,02±0,10
Tryptophan	0,47±0,02	1,09±0,05
Phenylalanine	1,10±0,06	2,55±0,20
Total	7,51±0,38	17,41±0,81
Non essentialamino acids		
Alanine	1,10±0,06	2,55±0,10
Aspartic acid	1,90±0,1	4,41±0,22
Histidine	0,60±0,03	1,39±0,07
Glycine	1,20±0,06	2,78±0,10
Glutamic acid	4,70±0,24	10,90±0,5
Proline	0,97±0,05	2,25±0,10
Serine	1,10±0,06	2,55±0,10
Tyrosine	0,87±0,04	2,02±0,10
Cysteine	0,44±0,02	1,02±0,05
Total	12,88±0,7	29,87±1,34

It was found (Table 3.6) that the total content of essential and non essential amino acids for sesame seeds is 7.51 and 12.88% respectively, and for sesame seeds concentrate - 17.41 and 29.87%. That is, a tendency to increase the content of amino acids by 131.82 and 131.91% respectively, relative to the content of sesame seeds.

For a more complete presentation of the biological value of seeds and sesame seeds concentrate, their amino acid score is presented. (Table 3.7). The most significant indicators of the biological value of the protein were established by the calculation method: by calculating the amino acid score, net protein utilization (NPU), protein quality index (I_{pq}) and biological value (BV).

Table 3.7

Characterization of biological value of sesame proteins

Name of amino acids	Scale of FAO/WHO, mg/g	Sesame seeds		Sesame seed concentrate	
		Content, mg/g	Score,%	Content, mg/g	Score,%
Isoleucine	40	46,39	115,98	46,44	116,11
Leucine	70	82,47	117,82	82,44	117,78
Lysine	55	34,54	62,79	34,44	62,63
Methionine	35	36,08	103,09	36,00	102,86
Phenylalanine	60	56,70	94,50	56,67	94,44
Threonine	40	44,85	112,11	44,89	112,22
Tryptophan	10	24,23	242,27	24,72	242,22
Valine	50	61,86	123,71	61,78	123,56
NPU	–	0,97		0,97	
BV,%	–	67,89		67,86	
I_{pq}	–	0,37		0,37	

From the given data in Table 3.7. it was found that the protein of seeds and sesame concentrate is not complete, because there are amino acids in which the value is less than 100%; such amino acids are methionine and phenylalanine. However, the net protein utilization and protein quality index for both samples are 0.97 and 0.37. The biological value for sesame seeds is 67.89% and for sesame seeds concentrate is 67.86%.

Solving the perspective task of creating a product of high biological value, it is advisable to present the characteristics of the amino acid composition of the proposed TF samples under the established TF storage conditions in three possible directions (Table 3.8).

Table 3.8

Characterization of the amino acid composition of TF

The name of the component	Contents, %					
	TF control sample			Developed TF sample with sesame seed concentrate		
	Freshly made	Storage temperature, °C		Freshly made	Storage temperature, °C	
		2±2	–18±2		2±2	–18±2
		after 15 days	after 4 months		after 15 days	after 4 months
Protein	5,00±0,25	5,00±0,25	5,08±0,25	5,10±0,26	5,10±0,26	5,16±0,26
Essential amino acids						
Valine	0,29±0,01	0,29±0,01	0,27±0,01	0,31±0,02	0,31±0,02	0,30±0,02
Histidine	0,12±0,006	0,12±0,006	0,14±0,007	0,14±0,007	0,14±0,007	0,15±0,007
Isoleucine	0,26±0,01	0,26±0,01	0,25±0,01	0,26±0,08	0,26±0,08	0,24±0,07
Leucine	0,43±0,02	0,43±0,02	0,45±0,02	0,44±0,01	0,44±0,01	0,47±0,01
Lysine	0,34±0,01	0,34±0,01	0,29±0,01	0,28±0,01	0,28±0,01	0,23±0,01
Methionine	0,11±0,006	0,11±0,006	0,09±0,005	0,15±0,008	0,15±0,008	0,14±0,007
Threonine	0,19±0,009	0,19±0,009	0,24±0,01	0,22±0,01	0,22±0,01	0,26±0,01
Tryptophan	0,06±0,003	0,06±0,003	0,08±0,004	0,09±0,005	0,09±0,005	0,1±0,005
Phenylalanine	0,23±0,01	0,22±0,01	0,20±0,01	0,26±0,01	0,26±0,01	0,24±0,01
Total	2,02±0,08	2,02±0,08	2,01±0,09	2,15±0,16	2,15±0,16	2,13±0,15
Non essentialamino acids						
Alanine	0,15±0,008	0,15±0,008	0,18±0,009	0,22±0,01	0,22±0,01	0,24±0,01
Asparagine	0,32±0,02	0,34±0,02	0,37±0,02	0,43±0,02	0,43±0,02	0,45±0,02
Glycine	0,09±0,005	0,09±0,005	0,12±0,006	0,20±0,01	0,20±0,01	0,22±0,01
Glutamic acid	0,95±0,05	0,9±0,05	1,04±0,05	1,09±0,05	1,09±0,05	1,15±0,06
Proline	0,42±0,02	0,42±0,02	0,45±0,02	0,35±0,02	0,35±0,02	0,40±0,02
Serine	0,26±0,01	0,24±0,01	0,26±0,01	0,27±0,02	0,27±0,02	0,31±0,02
Tyrosine	0,22±0,01	0,22±0,01	0,25±0,01	0,23±0,01	0,23±0,01	0,26±0,01
Cysteine	0,039±0,001	0,038±0,001	0,02±0,001	0,08±0,004	0,08±0,004	0,07±0,004
Total	2,40±0,12	2,39±0,12	2,69±0,13	2,87±0,14	2,87±0,14	3,10±0,15

It can be seen from Table 3.8 that the amino acid composition of the corresponding freshly made samples of TF and those samples that were stored for 15 days at 2±2 °C, has close values. However, these samples have differences in amino acid composition when stored at 2±2 °C for 15 days and –18±2 °C for 4 months. It should also be noted higher content of valine, histidine, leucine, threonine, phenylalanine, alanine, asparagine, glutamine and cystine in TF with sesame seed concentrate than in control TF.

Of course, the biological value of a protein depends not only on the number of essential amino acids, but also on their ratio to the reference protein: the greater their difference, the lower the balance and biological value [88; 137; 156]. The biological value is given for samples of TF, which were stored under the specified storage conditions in Table 3.9.

Table 3.9

Characterization of biological value of TF proteins

Name of amino acids	Scale of FAO/WHO, mg/g	TF control sample				Developed TF sample with sesame seed concentrate			
		Storage temperature, °C				Storage temperature, °C			
		2±2		–18±2		2±2		–18±2	
		after 15 days		after 4 months		after 15 days		after 4 months	
		Content mg/g	Score,%	Content mg/g	Score,%	Content mg/g	Score,%	Content mg/g	Score,%
1	2	3	4	5	6	7	8	9	10
Isoleucine	40	52,00	130,00	49,21	123,03	50,98	127,45	46,51	116,28
Leucine	70	86,00	122,86	88,58	126,55	86,27	123,25	91,09	130,12
Lysine	55	68,00	123,64	57,09	103,79	54,90	99,82	44,57	81,04
Methionine+cysteine	35	22,00	62,86	17,72	50,62	29,41	84,03	27,13	77,52
Phenylalanine+tyrosine	60	88,00	146,67	88,58	147,64	96,08	160,13	96,90	161,50
Threonine	40	38,00	95,00	47,24	118,11	43,14	107,84	50,39	125,97
Tryptophan	10	12,00	120,00	15,75	157,48	17,65	176,47	19,38	193,80
Valine	50	58,00	116,00	53,15	106,30	60,78	121,57	58,14	116,28
NPU	–	0,56		0,46		0,82		0,76	
BV,%	–	62,86		61,33		65,50		64,69	
I_{pq}	–	0,39		0,39		0,36		0,36	

According to the Table 3.9 it is established that all the proposed samples of TF have the lowest value of amino acid score in the ratio of methionine + cystine amino acids. Net protein utilization, biological value and protein quality index of TF control samples, stored under traditional conditions and frozen are 0.56, 62.86%, 0.39 and 0.46, 61.33%, 0, 39, respectively. The same indicators under the same storage conditions of TF samples with sesame seed concentrate are as follows: 0.82, 65.50%, 0.36 and 0.76, 64.69%, 0.36.

The following studies are devoted to the determination of fatty acid composition of scientific development (Table 3.10).

Table 3.10

Comparative characteristics of fatty acid composition of raw materials

Name of fatty acid	Content,% per 100 g	
	Sesame seeds	Sesame seed concentrate
Saturated		
Myristicacid $C_{14:0}$	0,12±0,004	0,001±0,00003
Palmitic acid $C_{16:0}$	4,44±0,22	0,36±0,02
Stearicacid $C_{18:0}$	2,09±0,10	0,17±0,009
Total, %	6,65±0,32	0,53±0,03
Unsaturated		
Palmitoleic acid$C_{16:1}$	0,15±0,008	0,01±0,0003
Oleic acid$C_{18:1}$	18,50±0,93	1,48±0,07
Linoleic acid$C_{18:2}$	21,37±1,1	1,70±0,09
Linolenic acid$C_{18:3}$	0,38±0,02	0,03±0,002
Total, %	40,40 ±2,06	3,22±0,17

According to the Table 3.10 there is a decrease in the total amount of fatty acids in the sesame seed concentrate: the total amount of saturated and unsaturated fatty acids for sesame seeds is 6.65 and 40.40% respectively , and the sesame seed concentrate is 0.53 and 3.22%.

In view of the destructive processes, the results of the study of the TF fatty acid composition were determined under the established storage conditions of the filling in three possible directions (Table 3.11). Studies of the fatty acids content of the TF proposed samples indicate a predominantly increased their content in the samples of the fillings with a sesame seeds concentrate. Such an increase is likely due to the chemical composition of the plant protein supplement and the partial replacement of non-fat dairy raw materials with concentrate.

Table 3.11

Characteristics of fatty acid composition of TF

Name of fatty acid	Content,% per 100 g					
	TF control sample			Developed TF sample with sesame seed concentrate		
	Freshly made	Storage temperature, °C		Freshly made	Storage temperature, °C	
		2±2	–18±2		2±2	–18±2
		after 15 days	after 4 months		after 15 days	after 4 months
Saturated						
Myristicacid $C_{14:0}$	0,0088±0,0004	0,009±0,0005	0,012±0,0006	0,009±0,0004	0,01±0,0005	0,015±0,0008
Palmitic acid $C_{16:0}$	0,02±0,001	0,02±0,001	0,03±0,001	0,22±0,01	0,25±0,01	0,30±0,02
Stearicacid $C_{18:0}$	0,01±0,0005	0,03±0,0001	0,1±0,005	0,10±0,005	0,12±0,006	0,22±0,01
Total, %	0,039±0,002	0,059±0,001	0,14±0,007	0,33±0,015	0,38±0,017	0,54±0,031
Unsaturated						
Palmitoleic acid $C_{16:1}$	0,004±0,0002	0,003±0,0001	0,001±0,00005	0,01±0,0005	0,007±0,0003	0,003±0,0001
Oleic acid $C_{18:1}$	0,02±0,001	0,02±0,001	0,015±0,0007	2,58±0,13	2,55±0,13	2,48±0,12
Linoleic acid $C_{18:2}$	0,003±0,0001	0,003±0,0001	0,002±0,0001	1,62±0,08	1,60±0,08	1,60±0,08
Linolenic acid $C_{18:3}$	0,1±0,005	0,1±0,005	0,05±0,002	0,03±0,002	0,02±0,001	0,02±0,001
Total, %	0,127±0,006	0,126±0,068	0,068±0,003	4,24±0,20	4,18±0,20	4,10±0,20

Table 3.12

Characteristics of the vitamin composition of TF

Name of vitamin	Content, mg/100 g	
	TF control sample	Developed TF sample with sesame seed concentrate
Water-soluble		
PP (nicotinic acid))	0,93±0,05	1,02±0,05
B_1 (thiamine)	0,04 ±0,002	0,18 ±0,009
B_2 (riboflavin)	0,22±0,01	0,17±0,009
B_5 (pantothenic acid)	0,06 ±0,002	0,03±0,001
B_6 (pyridoxine)	0,052±0,002	0,003±0,0001
B_9 (folic acid)	(0,62±0,03)·10^{-3}	(0,34±0,02)·10^{-3}
B_{12} (cyanocobalamin)	(0,05±0,002)·10^{-3}	(0,03±0,002)·10^{-3}
C (ascorbic acid)	0,48±0,024	0,27±0,01
H (biotin)	(0,40±0,02)·10^{-3}	(0,22±0,01)·10^{-3}
Total	1,78±0,09	1,67±0,08
Fat-soluble		
D (calciferol)	(0,0062±0,0003)·10^{-3}	(0,034±0,002)·10^{-3}
E (tocopherol)	0,98±0,05	0,84±0,04
K (phylloquinone)	–	(0,57±0,03)·10^{-3}
Total	0,98±0,05	0,84±0,04

The results of determining the vitamin composition (Table 3.12) indicate that the use of sesame seeds concentrate in the technology of TF promotes the appearance of vitamin K, increase the content of vitamin D, but the total amount of fat-soluble vitamins is reduced and for the control sample is 0.98 mg / 100 g, and for sample with concentrate - 0,84 mg / 100 g. The content of water-soluble vitamins in TF with sesame seed concentrate is less than the control sample, and is respectively 1,67 and 1,78 mg / 100 g.

No less valuable for human health are minerals. They significantly affect the structural characteristics of the products, which is caused by their interaction with the polysaccharide molecules [138]. In order to identify and find out their quantity, the characteristics of the mineral composition of the scientific development are given (Table 3.13).

Table 3.13

Characteristics of the mineral composition of TF

The name of the element	Content, mg/100 g	
	TF control sample	Developed TF sample with sesame seed concentrate
1	2	3
Macroelements		
Calcium	150,90±7,54	263,45±13,20
Magnesium	19,58±0,98	86,25±2,50
Sodium	59,24±2,96	68,60±2,00
Potassium	145,98±7,29	207,96±10,40
Phosphorus	110,08±5,50	199,86±10,00
Chloride	12,81±0,64	12,81±0,40
Total	498,59±25,21	838,88±38,50
Microelements		
Iron	0,28±0,01	2,27±0,1
Zinc	0,05±0,002	0,05±0,002
Iodine	$(1,05\pm0,06)\cdot10^{-3}$	$(0,1\pm0,003)\cdot10^{-3}$
Copper	$(1,4\pm0,07)\cdot10^{-3}$	$(1,4\pm0,07)\cdot10^{-3}$
Manganese	$(0,7\pm0,02)\cdot10^{-3}$	$(0,7\pm0,02)\cdot10^{-3}$
Selenium	0,23±0,01	0,23±0,01
Fluorine	$(2,33\pm0,12)\cdot10^{-3}$	$(2\pm0,08)\cdot10^{-3}$
Total	0,56±0,02	2,55±0,11

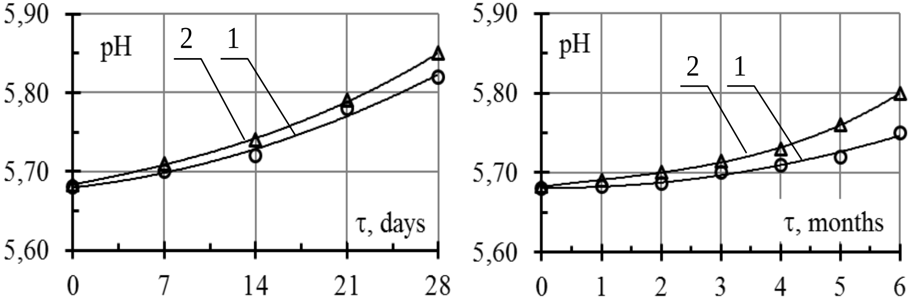
Table 3.13 shows that the content of minerals in the TF sample with the addition of sesame seeds concentrate relative to the control sample is increased about twice, in particular, a significant increase in the content of calcium, magnesium, potassium, phosphorus and iron.

Drawing general conclusions about the chemical composition of TF, we can note the positive effect of sesame seed concentrate on the biological value of the developed products, vitamin and mineral composition.

3.4 Study of physicochemical properties of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

3.4.1Study of chemical changes

Chemical and biochemical processes play a major role in TF technology: they affect product readiness and shelf life. During storage, the filling undergoes a series of transformations that occur under the influence of oxidation processes. The product changes its acidity, which directly affects its organoleptic properties. In view of this, studies to determine the pH (active acidity) of TF are relevant (Fig. 3.2).



a) b)

Fig. 3.2. Dependence of the TF active acidity on the storage duration at temperature: a) 2±2 °C; b) -18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seed concentrate

In Fig. 3.2 shows that under different storage conditions there is an increase in the active acidity in the test samples of TF, and the presence of a sesame seed concentrate in the recipe composition of TF promotes an increase in the active acidity of the product. This is probably due to the tendency of the plant protein supplement itself to oxidize due to the presence of approximately 10% fat in the concentrate.

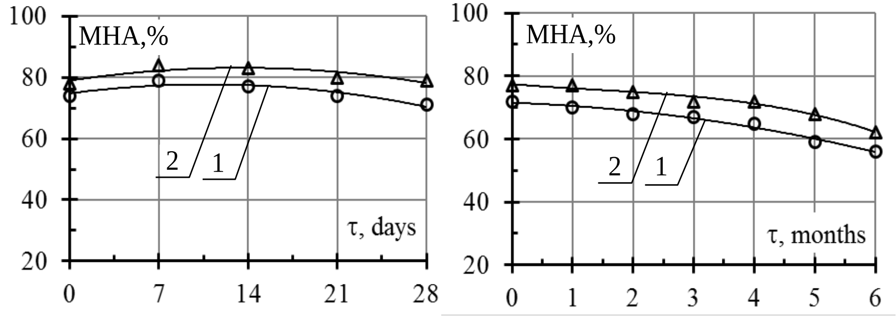
As shown in Fig. 3.2 (a), in TF samples, stored at 2±2 °C, a steady increase in active acidity was observed during the first 14 days. Then the rate increased rapidly enough, which may indicate food unsuitability of a product. In Fig. 3.2 b) it is seen that the active acidity of the TF control samples and the samples of the filling with sesame seed concentrate increased steadily during the first 4 months of low temperature storage. After 4 months, the active acidity of both fillings changed more intensively.

Considering the results of the active acidity study of the proposed TF samples under different storage conditions, the following rational storage periods can be recommended: at 2±2 °C for 14 days and at –18±2 °C for 4 months. It is worth noting that the recommended shelf life, taking into account changes in active acidity, does not contradict previous studies.

3.4.2 Study of changes in moisture connection forms

3.4.2.1 Study of moisture-holding ability

An important criterion for the quality of TF is the ability of the prescription components to retain moisture throughout the shelf life. This property helps to reduce technological costs and allows to obtain a filling with a gel-like gentle and plastic consistency [237; 257; 262; 272; 273; 284]. Therefore, there was a need to investigate the moisture-holding ability of TF. In Fig. 3.3. shows changes in the MHA index of TF under different storage conditions.



a) b)

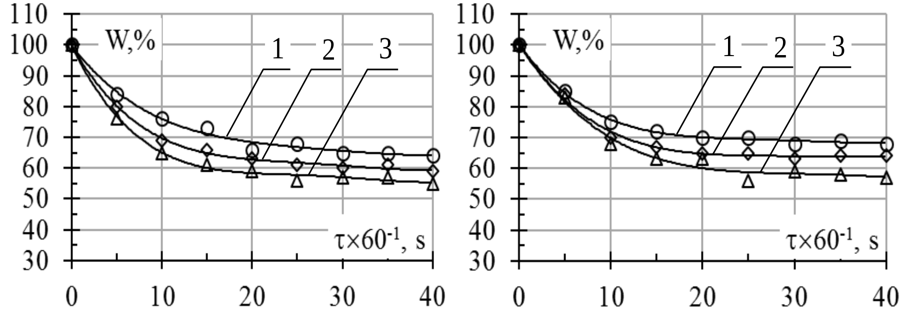
Fig. 3.3. Dependence of moisture-holding ability of TF on the storage duration at temperature: a) 2±2°C; b) –18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seed concentrate

In Fig. 3.3 it is shown that sesame seed concentrate as a prescription ingredient of TF promotes higher MHA of the development. The trends of MHA change in both samples are similar. It is probable that the increase of MHA in the presence of sesame seed concentrate in the system is due to the additional ability to hydratation of plant proteins and polysaccharides, which was established by previous studies of the functional and technological properties of plant protein additives. A decrease of MHA indicates a decrease in the strength of the intermolecular interactions of the formulation components and the release of moisture, which is more relevant after defrosting of the samples when the product structure is "traumatized" by ice crystals [16; 31; 67; 135; 222].

3.4.2.2 Determination of changes in product humidity relative to the time of high temperature action

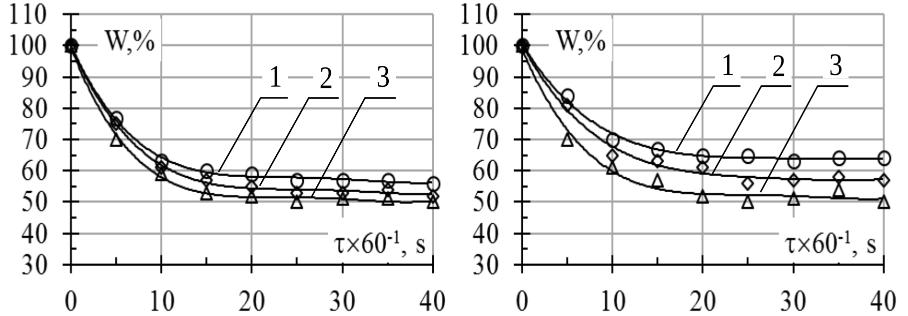
The different nature and chemical composition of the formulation ingredients of TF affect on the content and ratio of free and bound moisture. As it is found that MHA of TF decreases during storage, it becomes necessary to determine how much moisture is associated with the ingredients of filling . It is known that the weaker the bound moisture, the more intense the spoilage process in the product occur. Free moisture is easily removed by drying. It should also be noted that as the temperature rises, the water molecules move randomly, resulting in a break in hydrogen bond [267].

Moisture content was determined by thermogravimetric method with the help of scales-hydrometers at a constant temperature of 160°C (Fig. 3.4 та 3.5).



a) b)

Fig. 3.4. Humidity dependence of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature 2±2°C on duration of high-temperature processing: 1 - freshly made sample; 2 - sample after 14 days of storage; 3 - sample after 28 days of storage



a) b)

Fig. 3.5. Humidity dependence of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature –18±2°C on duration of high-temperature processing: 1 - freshly made sample;2 - sample after 3 months of storage; 3 - sample after 6 months of storage

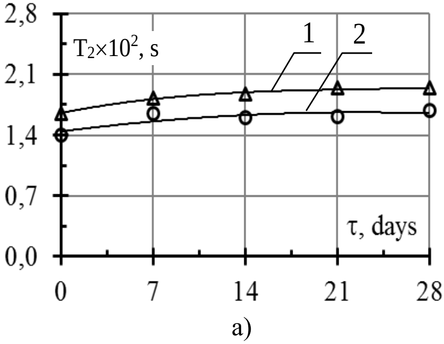
For TF is characteristic that its control samples are faster reaching constant humidity than those with sesame seeds concentrate, that is, they are dried more quickly. This tendency is true for TF samples which stored under traditional conditions and for the filling samples that have been frozen (Figs. 3.4 and 3.5). Thus, it has been found that plant protein supplement promotes moisture retention. With regard to freezing, it has a negative effect on the TF structure: TF samples after defrosting are dried faster than similar samples stored under traditional conditions.

It was also found that for TF, which stored under two different conditions, storage adversely affected the ability to hold moisture. With regard to changes in the humidity of TF, depending on the time of high temperature action, the following can be stated. First, it was found that the presence of sesame seeds concentrate slows the removal of free moisture. Secondly, it can be seen that the longer the product is stored under traditional conditions and at low temperatures, the more free moisture it has. And freezing leads to destruction of the structure [16; 31; 67; 135; 222]. Studies conducted to study the changes in humidity of TF depending on the time of high temperature action confirm the data obtained from the study of MHA.

3.4.2.3 Determination of moisture condition

A characteristic feature of free moisture is not only its ability to act as a solvent, but also its inherent high mobility, which can be determined by spin echo method - nuclear magnetic resonance [27; 30; 149; 173; 222; 245]. During the study, particular attention was paid to the chemical composition of TF samples, since the chemical composition affects the rate of energy redistribution in the spin-spin system and is characterized by spin-spin interaction and molecular mobility of water. It should be noted that the spin-spin relaxation time (T_2) depends on the mobility of the protons that make up the water molecule; the length T_2 increases with the mobility of protons.

Also, the temperature modes of storage have a great influence on the change in the moisture state. Thus, control TF and TF with sesame seed concentrate were stored under two temperature conditions studied: under traditional conditions (2±2 °C) for 28 days and in a frozen state (-18±2 °C) for 6 months. Figure 3.6 (b) shows the effect of freezing on the change in spin-spin relaxation which characterizing the molecular mobility of moisture, thereby indicating the free moisture in the TF samples with different content of dairy and plant components during low-temperature storage.



a) b)

Fig. 3.6. Dependence of spin-spin relaxation time (T_2) of TF on the duration of storage at temperaturea) 2±2°C andb) –18±2°C: 1 - TF control sample; 2 - developed TF sample with sesame seed concentrate

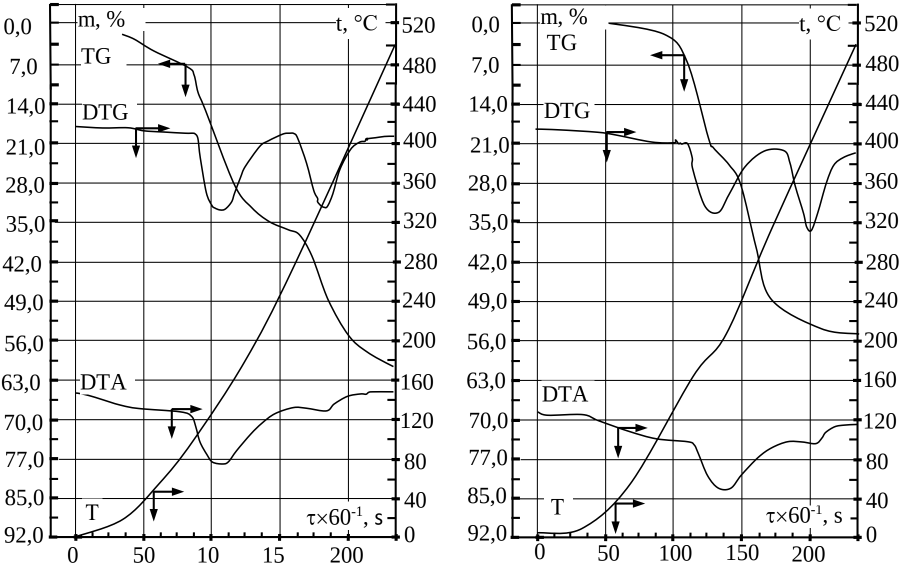
The results of the studies presented in Fig. 4.6, indicate that at storage temperatures of 2±2 °C and –18±2 °C of the TF samples, the spin-spin relaxation time (T_2) increases in the TF control relative to TF with the sesame seed concentrate. Thus, for a freshly made TF control sample (Fig. 3.6 a) and after 28 days of storage at a temperature of 2±2°C T_2 changes from 0.0171 to 0.0194 s, and for the developed TF sample with concentrate - from 0.0147 to 0.0170 s.

Freezing does not significantly affect the change in relaxation time. In the study of spin-spin relaxation of the dipoles of water of TF, it is found that the time of spin-spin relaxation of TF increases during storage, which indicates the loosening of the structure and the release of free moisture. Freezing does not significantly affect the time of spin-spin relaxation. The lowest values of T_2 are inherent in TF with sesame seed concentrate. This confirms the growth of MHA in the filling with sesame seeds concentrate, as noted above.

3.4.2.4 Study of kinetic regimes of endothermic processes

Previous research has shown that by using in the TF formulation of sesame seed concentrate, low-esterified citrus pectin and modified corn starch, bound moisture prevails. Bound moisture, unlike free moisture, is characterized by difficulty in removal, since it requires a high temperature, accompanied by absorption (endothermic conversion) or allocation of heat (exothermic conversion). Thus, physico-chemical changes in the TF occur, in particular changes of mass during the action of temperature.

The kinetic parameters of endothermic processes in TF were investigated using differential thermal analysis (DTA) on a derivatograph. The essence of the method is the assumption that at given the constant rate of heating, the value of the mass change degree or heat absorption by the system in the region of fixed onset and maximum process development is proportional to the conversion rate constant for each temperature value. Moisture bonding patterns were determined by analyzing the curves of change in mass (TG), differential thermogravimetry (DTG and DTA) and temperature (T) [152] (Figs. 3.7 and 3.8).



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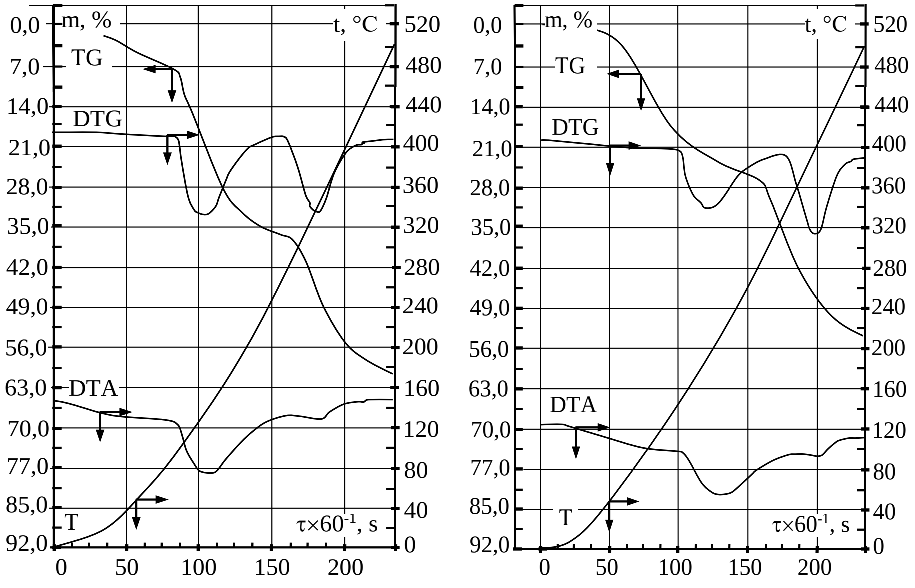
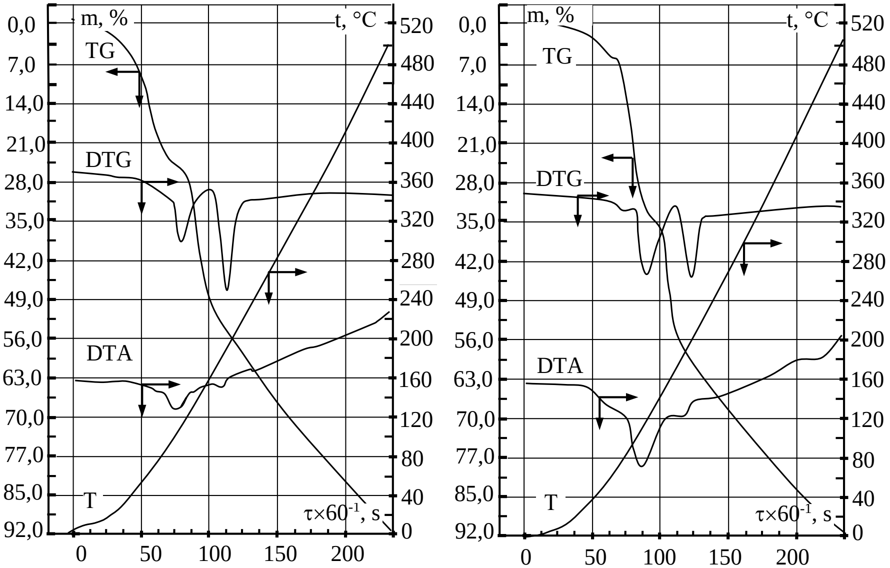
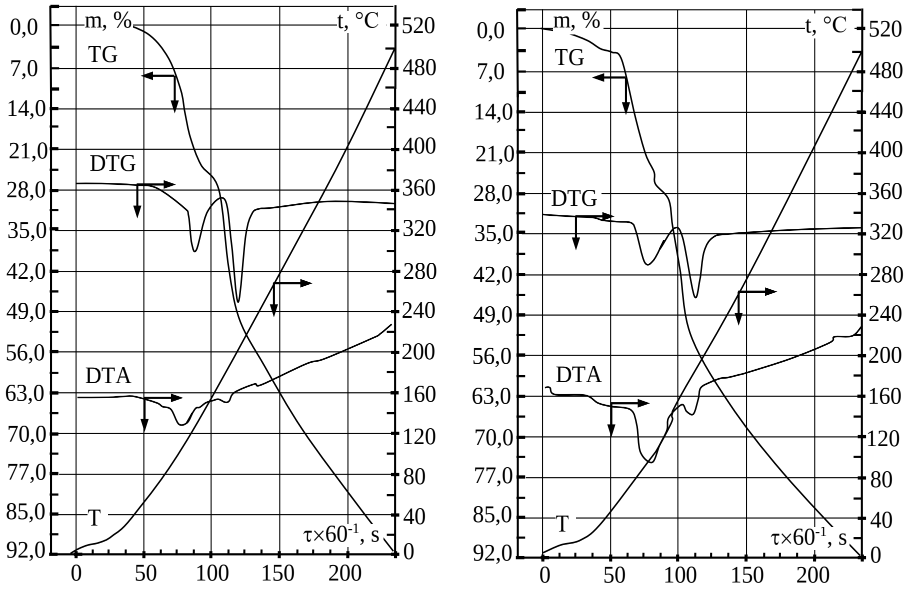


c) d)

Fig. 3.7. Studying of endothermic processes kinetic parameters of TF control sample: a) freshly made; b) after 15 days of storage at 2±2 °C; c) freshly made defrozen; d) after 4 months of storage at a temperature of −18±2°C



a) b)



c) d)

Fig. 3.8. Studying of endothermic processes kinetic parameters of TF with sesame seed concentrate: a) freshly made; b) after 15 days of storage at 2±2 °C; c)freshly made defrozen; d) after 4 months storage at −18±2°C

In Fig. 3.7 and 3.8 show different dynamics of moisture loss with increasing temperature influence on TF, which indicates about different forms of moisture connexion in it. Thus, according to the experimental DTG curves indicating the amount of moisture loss (TG) under a given temperature influence (T), three peaks of the endothermic process of mass removal of moisture from the TF were recorded. The maximums (peaks) of moisture mass loss at temperature in the TF, which determine the origin of the bond and characterize the moisture bond form are given in Table. 3.14.

Table 3.14

Characterization of maxima of TF mass loss

TF sample		Temperature maximum, °C	The amount of moisture released			
			Free		Bound	
			%	mg	%	mg
1	2	3	4	5	6	7
TF control	Freshly made	I stage				
		100±2	6,0±0,5	30,0±0,5	–	–
		II stage				
		120±2	–	–	16,0±0,5	80,0±0,5
		173±2	–	–	30,0±0,5	150,0±0,5
		206±2	–	–	41,0±0,5	205,0±0,5
		III stage				
		235±2	–	–	53,0±0,5	265,0±0,5
	Freshly made (defrozen)	I stage				
		100±2	6,5±0,5	32,5±0,5	–	–
		II stage				
		120±2	–	–	23,0±0,5	115,0±0,5
		173±2	–	–	33,0±0,5	165,0±0,5
		195±2	–	–	42,0±0,5	210,0±0,5
		III stage				
		234±2	–	–	55,0±0,5	275,0±0,5
	After 15 days of storage at 2±2 °C	I stage				
		89±2	6,0±0,5	30,0±0,5	–	–
		II stage				
		115±2	–	–	25,0±0,5	100,0±0,5
		167±2	–	–	35,0±0,5	175,0±0,5
		198±2	–	–	45,0±0,5	225,0±0,5
		III stage				
		225±2	–	–	56,0±0,5	280,0±0,5
	After 4 months storage at −18±2°C	I stage				
		86±2	8,0±0,5	40,0±0,5	–	–
		II stage				
		110±2	–	–	25,0±0,5	100,0±0,5
		164±2	–	–	40,0±0,5	200,0±0,5
		195±2	–	–	47,0±0,5	235,0±0,5

Continuation of Table 3.14

1	2	3	4	5	6	7
		III stage				
		223±2	–	–	58,0±0,5	290,0±0,5
Developed TF sample with sesame seed concentrate	Freshly made	I stage				
		105±2	–	–	8,0±0,5	40,0±0,5
		II stage				
		177±2	–	–	24,0±0,5	120,0±0,5
		205±2	–	–	35,0±0,5	175,0±0,5
		III stage				
		245±2	–	–	48,0±0,5	240,0±0,5
	Freshly made (defrozen)	I stage				
		103±2	–	–	10,0±0,5	50,0±0,5
		II stage				
		170±2	–	–	24,0±0,5	120,0±0,5
		200±2	–	–	36,0±0,5	180,0±0,5
		III stage				
		243±2	–	–	50,0±0,5	250,0±0,5
	After 15 days of storage at 2±2 °C	I stage				
		98±2	3,0±0,5	15,0±0,5	–	–
		II stage				
		120±2	–	–	12,0±0,5	60,0±0,5
		175±2	–	–	24,0±0,5	120,0±0,5
		203±2	–	–	36,0±0,5	180,0±0,5
		III stage				
		240±2	–	–	48,0±0,5	240,0±0,5
	After 4 months storage at −18±2°C	I stage				
		98±2	7,0±0,5	35,0±0,5	–	–
		II stage				
		115±2	–	–	19,0±0,5	95,0±0,5
		170±2	–	–	32,0±0,5	160,0±0,5
		200±2	–	–	44,0±0,5	220,0±0,5
		III stage				
		240±2	–	–	55,0±0,5	275,0±0,5

The first stage, which causes the beginning of moisture removal from the TF control for a freshly made sample and freshly made immediately after defrosting, occurs at a temperature of 100±2°C, as after 15 days and as 4 months of storage. During the second stage of endo-effects in these TF samples removes the moisture inherent in the bound moisture, as are the maximums of the same samples in the third stage, which causes the final destruction of the structure due to significant moisture loss. Thus, it was found that the highest loss of moisture was experienced by the TF samples after storage under both regimes, which is probably due to the ability of the starch to retain moisture, but retrogradation (aging) occurs. In this case, the moisture during storage is bound by pectin and other prescription components with hydrophilic properties (the action of starch is weakened). This causes a decrease of temperature influence for the destruction of certain chemical bonds between the TF prescription components during storage.

Summarizing the results of experimental studies to study the kinetic parameters of endothermic TF processes, the following conclusion can be drawn. Sesame seed concentrate contributes to the resistance of TF to high temperatures and reduces moisture mass loss. For both TF which stored under freezing, the peaks indicate a greater susceptibility to the removal of bound moisture in such samples. Moisture mass losses are more significant for TF samples (control) which were storaged at low temperature.

3.4.2.5 Determination the amount of frozen moisture

An important role during the TF storage is played the mass fraction of moisture in the filling, which characterizes the consistency, determines the physical, chemical and structural-mechanical properties throughout the shelf life [99; 131; 142; 178].

Moisture bonding forms, including the amount of free and bound moisture, were investigated using a low-temperature calorimetric method. Its essence is to record the heat released during the phase transition of water to ice [27; 175; 178; 239; 256]. As is known, only free moisture is involved in the phase transition. It is in the free state of intercellular space and easily freezes, unlike bound moisture. With its freezing, the concentration of salts in the intercellular solution increases, which causes the cryoscopic temperature to shift to a lower one. The freezing of moisture occurs gradually, until a continuous solid mass is reached, called eutectic [39; 163; 178; 266]. The change in the amount of free moisture in TH during storage under traditional conditions is shown in Fig. 3.9. It is not advisable to carry out such studies for filling which has already been exposed to low temperatures (freezing and storage at –18±2 °C).

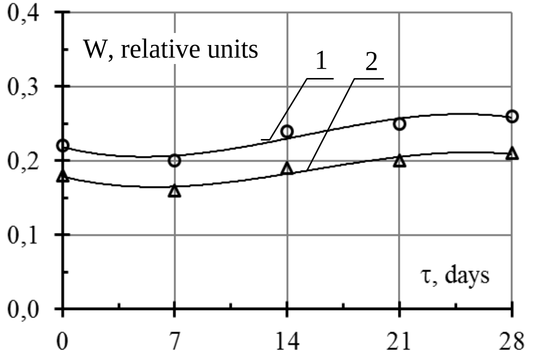


Fig. 3.9. Dependence of the content of freezed (free) moisture TF on storage time: 1 - TF control sample; 2 - developed TF sample with sesame seeds concentrate

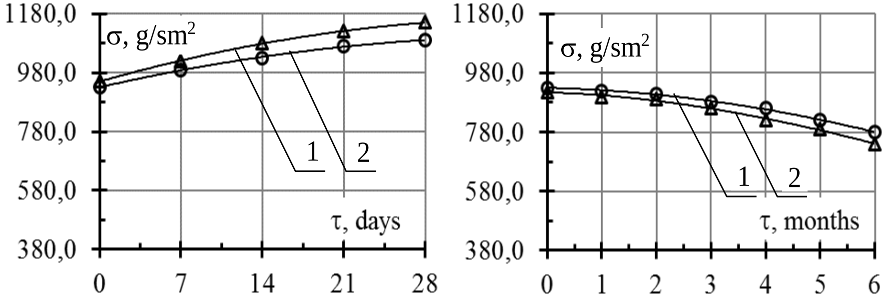
In Fig. 3.9 shows that the amount of frozen (free) moisture in the TF during the whole storage period increases. Such an increase of the free moisture content in the TF indicates damage to the structure and the weakening of interactions between the recipe components that are activated over time. It is revealed that during storage in TF with a plant additive less freezed moisture is released. Thus, it was found that the amount of frozen moisture depends on the formulation composition of TF: the presence in their recipe composition of the concentrate has a positive effect on the occurrence of intermolecular interactions between the ingredients, which is due to a decrease in frozen moisture.

Summarizing the above, the results of the study of the physicochemical properties of the proposed thermostable filling using dairy raw material and sesame seeds concentrate can be presented in two directions. The first area concerns the plant protein supplement and proves the feasibility of its use in TF technology. Thus, sesame seeds concentrate contributes to: increase of MHA, moisture retention, reduction of weight loss and amount of free moisture. The second direction - freezing - is manifested in a slight decrease of MHA and the destruction of the structure, a greater susceptibility to the removal of moisture.

3.5 Study of rheological properties of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

3.5.1 Determination of strength

One of the important indicators that determines the changes in the properties of TF throughout the shelf life is the strength indicator. In particular, the influence of low temperature on the texture properties of the product leads to certain negative changes: as a result of the destructive action of ice crystals, the structure of TF after defrosting is disturbed and loosened, and moisture is lost. With the help of the Valent device, the strength of the proposed TF samples was determined (Fig. 3.10).



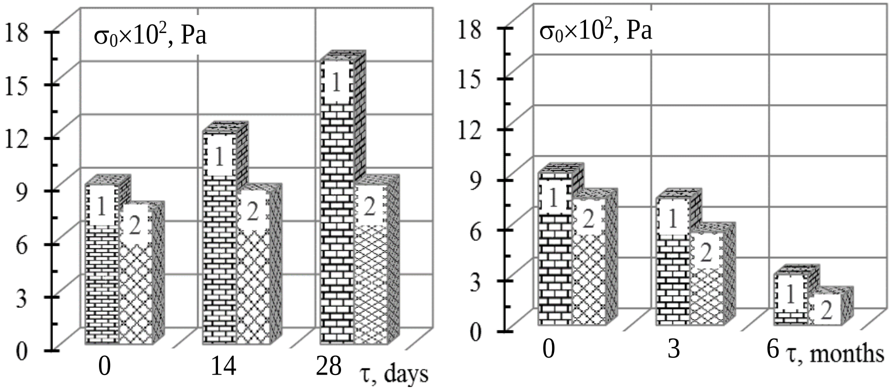
a) b)

Fig. 3.10. Dependence of TF strength on the duration of storage at a temperature: a) 2±2°C; b) –18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seeds concentrate

The results of the strength study show that TF samples with the addition of sesame seed concentrate at storage temperatures of 2±2 and –18±2 °C have slightly lower values of strength than similar samples without concentrate. Also in the course of data analysis Fig. 3.11 it was proved the strength of the test samples with a shelf life of 28 days at 2±2 °C was increased, and in the case of storage at –18±2 °C for 6 months, the indicators decreased.In case of TF samples storage at -18±2 °C for 6 months, there is a slight decrease in the strength indicator, mainly during the first 4 months: for the control and developed TF this indicator after 4 months is 862.5 and 855 g/cm^2, respectively, and after 6 months - 800 and 792.5 g/cm^2. The established change in the strength of TF indicates that the presence in the TF composition of sesame seeds concentrate helps to reduce the strength of the filling and gives a more plastic consistency; this is confirmed by subsequent studies.

3.5.2 Determination of the shear stress

The studies were performed on a penetrometer, which allows to measure the amount of the product deformation during the stress on it. According to the obtained values, the limiting shear stress of TF under different storage regimes was determined by the calculation method (Fig. 3.11).



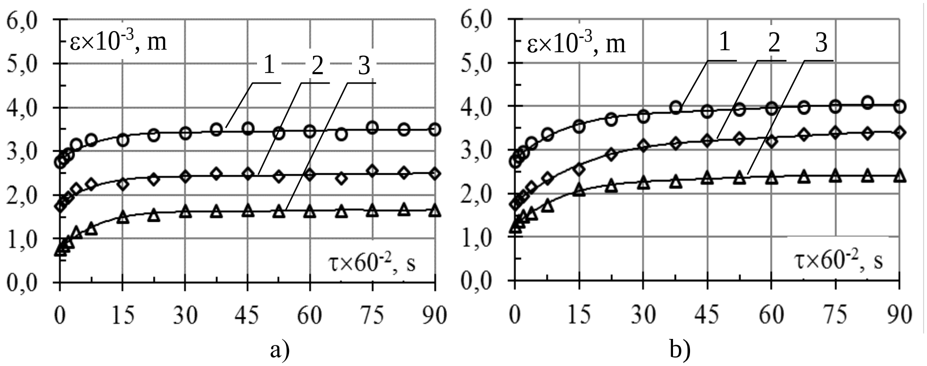
a) b)

Рис. 3.11. Dependence of the maximum shear stress of TF on the duration of storage at temperatures:a) 2±2°C; b) –18±2 °C; 1 - TF control sample; 2 - developed TF sample with sesame seeds concentrate

In Fig. 3.11 shows a decrease in the shear stress of the TF samples with the addition of a sesame seed concentrate, i.e. a decrease in their resistance. From the results of determining the shear stress, it can be stated that at low storage temperatures, the TF samples lose their resistance to deformation action; this indicates the destruction of the structure. TF with sesame seed concentrate has less resistance, which contributes to the formation of a softer structure. The trend identified is probably related to the structure, absorption and retention properties of moisture, the presence of a large number of hydrophilic and hydrophobic groups in the case of the combined use of dairy and plant components.

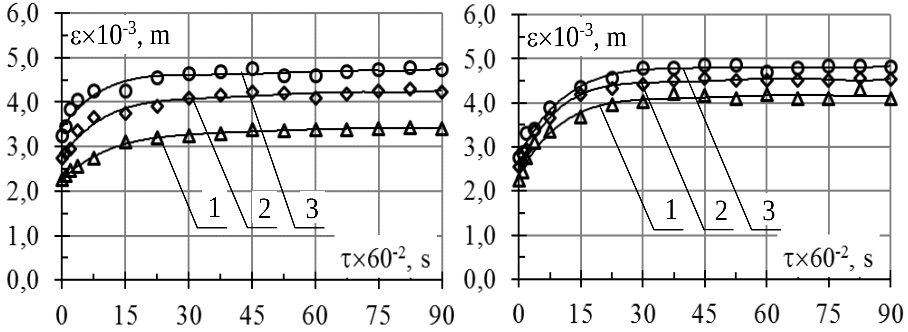
3.5.3 Study of structural and mechanical properties

Much of the rheological parameters of the proposed filling can be determined during mechanical loading. During loading, the TF samples are deformed and subjected to a certain stress, which is the integral beginning of the forces of internal interaction of the recipe components with each other. According to A.P. Rebinder's classification, dispersed, colloidal and high molecular systems are divided into liquid and solid. In view of this, TF has the properties of a solid body. As you know, such bodies are characterized by certain indicators: elasticity, plasticity, strength and other characteristic properties, which are determined by the relative deformation of the product during the stress for a certain time. These changes in the structural and mechanical parameters of the TF during storage under different conditions are shown in Tables 3.15 and 3.16 and in the form of creep deformation curves of the prototypes (Figs. 3.12 and 3.13).



a) b)

Fig. 3.12. Dependence of relative compression deformation of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature 2±2°C on the time of stress: 1 – freshly made sample; 2 – sample after 14 days of storage; 3 – sample after 28 days of storage



a) b)

Fig. 3.13. Dependence of relative compression deformation of a) TF control sample and b) developed TF sample with sesame seed concentrate at storage temperature -18±2°C on the time of stress: 1 – freshly made sample; 2 – sample after 3 months of storage; 3 – sample after 6 months of storage

Table 3.15

Structural-mechanical characteristics of TF at storage temperature 2±2ºC

Name of indicator	TF control sample			Developed TF sample with sesame seed concentrate		
	Duration of storage at temperature 2±2°C, days					
	0	14	28	0	14	28
Reverse deformation ($\gamma_{rd.}$), m×10^3	3,37	2,24	1,66	3,84	3,20	2,32
Irreversible deformation ($\gamma_{ird.}$), m×10^3	0,04	0,18	0,11	0,18	0,18	0,18
Total deformation (γ_{td}), m×10^3	3,40	2,42	1,77	4,02	3,38	2,50
Shear stress (τ), Pa	1498,86	1498,86	1498,86	1498,86	1498,86	1498,86
Pliability (I), Pa^{-1}×10^6	2,27	1,61	1,18	2,68	2,25	1,67
Conditionally instantaneous modulus of flexability (G_f), Pa×10^{-5}	5,93	9,86	15,36	5,26	7,04	11,42
High elastic module (G_{el}), Pa×10^{-5}	17,84	20,93	21,91	15,17	14,03	14,92
Plastic viscosity (η^*_0), (Pa×s)×10^{-9}	225,00	45,00	74,90	45,00	45,00	45,00
The ratio of deformation inverse to total (K)	0,99	0,93	0,94	0,96	0,95	0,93
Viscosity of elastic aftereffect (η_{el}), (Pa×s)×10^{-7}	62,45	97,75	102,19	86,47	62,45	72,53
Relative flexability (Fl), %	74,27	62,91	55,20	70,92	63,03	52,56
Relative plasticity (Pl), %	1,06	7,45	6,11	4,48	5,33	7,21
Relative elasticity (El), %	24,68	29,64	38,69	24,60	31,54	40,22
Relaxation period (Θ), s×10^{-3}	505,20	67,08	83,00	115,08	95,88	69,48

Table 3.16

Structural-mechanical characteristics of TF at storage temperature -18±2º C

Name of indicator	TF control sample			Developed TF sample with sesame seed concentrate		
	Duration of storage at temperature –18±2°C, months					
	0	3	6	0	3	6
Reverse deformation ($\gamma_{rd.}$), m×10^3	3,26	4,14	4,54	4,20	4,48	4,66
Irreversible deformation ($\gamma_{ird.}$), m×10^3	0,11	0,07	0,07	0,18	0,18	0,11
Total deformation (γ_{td}), m×10^3	3,37	4,21	4,61	4,38	4,66	4,77
Shear stress (τ), Pa	1498,86	1498,86	1498,86	1498,86	1498,86	1498,86
Pliability (I), Pa^{-1}×10^6	2,25	2,81	3,07	2,92	3,11	3,18
Conditionally instantaneous modulus of flexability (G_f), Pa×10^{-5}	7,77	4,85	4,20	4,79	4,53	4,29
High elastic module (G_{el}), Pa×10^{-5}	11,25	14,30	15,48	14,09	12,88	12,79
Plastic viscosity (η^*_0), (Pa×s)×10^{-9}	74,90	112,00	112,00	45,00	45,00	74,90
The ratio of deformation inverse to total (K)	0,97	0,98	0,98	0,96	0,96	0,98
Viscosity of elastic aftereffect (η_{el}), (Pa×s)×10^{-7}	37,47	49,96	72,53	41,25	48,88	40,87
Relative flexability (Fl), %	57,24	73,38	77,43	71,57	71,13	73,15
Relative plasticity (Pl), %	3,21	1,71	1,56	4,11	3,87	2,27
Relative elasticity (El), %	39,55	24,90	21,01	24,31	25,00	24,58
Relaxation period (Θ), s×10^{-3}	163,00	310,20	340,20	125,88	134,28	233,00

In Fig. 3.12 it can be seen that during the storage of TF under the traditional conditions, the samples become less fluid, compacted, probably due to on the one hand, to the redistribution of moisture if the bonds are stabilized and, on the other due to syneresis. Instead, tthe fluidity for the corresponding samples (depending on the storage time) stored in the frozen state is increased (Fig. 3.13). This is due to the "loosening" of the structure by the negative influence of ice crystals. In general, it can be argued that freezing contributes to increased fluidity.

However, due to the analysis of changes in the structural and mechanical characteristics of the TF during deformation, the difference between them during storage at a temperature of -18±2°C was established. Thus, during the comparison of the TF sample freshly made (it was frozen and immediately unfreez) and after 6 months of storage the increase of the deformation curves is revealed. This trend is true only for samples stored in a frozen state. Such a change is likely to be caused by the effect of low temperature on the change in the moisture state, which in turn affects the structure of the filling.

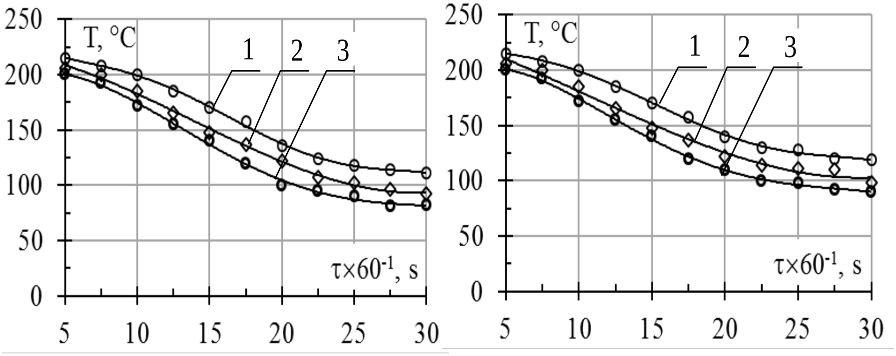
Summarizing the data on the change in the rheological properties of TF with different formulations and the influence of freezing, we can state the following. TF samples during storage at a traditional temperature acquire a strong and dense structure, probably due to the physico-chemical changes in the interactions between the recipe components. It was found that a TF sample with a plant protein supplement had a more uniform change in storage curves and a softer structure, as evidenced by the deformation curves. Opposite changes have low-temperature TF samples for 6 months. As is known, during storage in a frozen state, moisture enters a crystalline state, and crystals of different sizes are formed, resulting in the possibility of damage to the structure. Therefore, after defrosting the filling, there is a softening of its structure, the so-called "loosening".

3.6 Determination of the temperature influence on the technological properties of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

Of course, the thermal influence is a particular importance in the manufacture of thermostable filling. Temperature causes changes in heat exchange, physico-chemical, structural-mechanical and technological properties of the food system. Because of the temperature influence, strong chemical bonds can be broken. All of this leads to the rearrangement of the component molecules and the formation of new bonds. As you know, thermostable filling is characterized by a structure that does not change its physicochemical and, in particular, texture properties with a temperature action of about 200 °C for (10…15)×60 s [69; 70; 71; 93; 214; 215].In the course of the experimental studies, in particular the establishment of moisture bound forms, the positive effect of sesame seed concentrate on a number of physicochemical properties of the filling was revealed. Thus, the concentrate promotes moisture retention and increases the moisture-holding ability of the product. Therefore, it is advisable to find out what effect the sesame seed concentrate has on the technological properties of the developed filling.

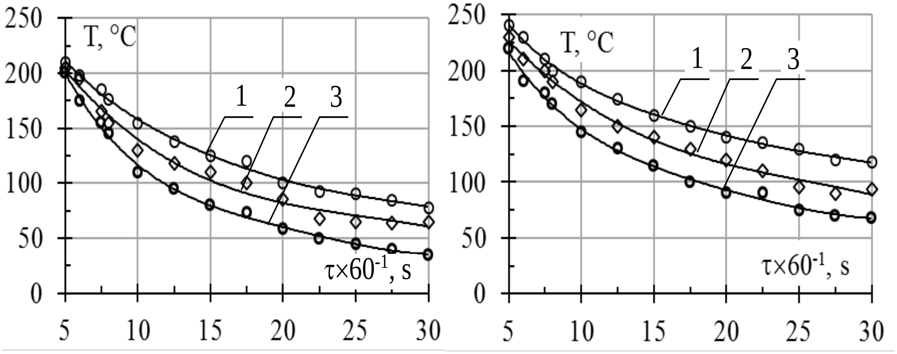
3.6.1 Change of thermal resistance

One of the main technological properties in the production of thermostable filling using dairy raw materials and sesame seeds concentrate is thermalstability, which means the temperature action that the product can withstand without changing its properties. To detect the thermostable properties, the duration of the action of temperature in the range of 100…220°C for filling samples with different formulations, which were stored under different conditions was studied.The dependence of thermal stability on temperature (τ = f (t)) has an inverse dependence. The thermal stability of the TF samples stored at 2±2 °C was determined immediately after manufacture, on the 14th and 28th day of storage (Fig. 3.14). However, the thermal stability of TF samples stored at –18±2 °C was investigated immediately after manufacture, on the 3rd and 6th month of storage (Fig. 3.15).



a)　　　　b)

Fig. 3.14. The dependence of thermal stability a) TF control sample and b) the developed TF sample with sesame seeds concentrate at a storage temperature of 2±2 °C on the influence of high-temperature processing: 1 – freshly made sample; 2 – sample after 14 days of storage; 3 – sample after 28 days of storage



a) b)

Fig. 3.15. The dependence of thermal stability a) TF control sample and b) the developed TF sample with sesame seeds concentrate at a storage temperature of –18±2°C on the influence of high-temperature processing: 1 – freshly made sample; 2 – sample after 3 months of storage; 3 – sample after 6 months of storage

According to Fig. 3.14 and 3.15, there is an intense decrease in the thermal stability of all TF samples during storage under both conditions, indicating syneresis.

Freezing has been shown to reduce the thermal stability of the filling. Probably, as a result of the transition of free moisture to the crystalline state during storage of TF at –18 ± 2 °C, ice crystals of various sizes are formed, which cause damage to the structure of the filling. This explains the slight decrease in thermal stability, since it reduces the connexion strength between the recipe components [16; 31; 67;93 135; 220].

Comparing the data of Figures 3.14 and 3.15, the undeniable positive effect of sesame seed concentrate - a plant protein supplement increases the thermal stability of TF can be noted. This means that the developed filling, which contains in its recipe composition of sesame seeds concentrate, experiences less negative changes in its properties than the product without plant protein additives. This indicates the formation in the developed TF sample with sesame seed concentrate stronger interactions between the recipe components: high thermal stability is likely due to the action of intermolecular interaction forces, namely the increase of the interaction of surface layers and base phases [90; 233].

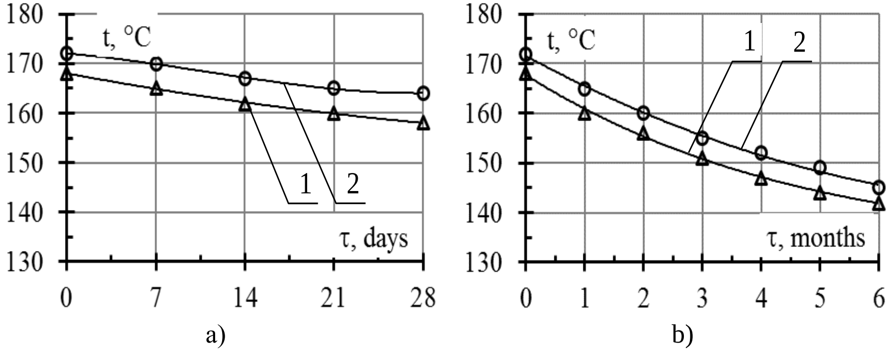
Therefore, it is established that the highest values of thermal stability have developed thermostable filling with sesame seeds concentrate. The results of the thermal stability study of the developed TF samples with concentrate after defrosting (freshly made, after storage for 3 and 6 months) are characterized by a similar trend of change of the indicator.

The above trend is also characteristic for filling control samples. Carrying out control samples of filling which stored under traditional conditions, then for a freshly made control sample of TF the thermal stability decreases from 28×60 to 11×60 s; for the sample examined for the 14th day, from 25×60 to 9×60 s; for the sample examined on the 28th day, from 20×60 to 7×60 s. Changes in the thermal stability of the control samples stored in the frozen state (fresh, after storage for 3 and 6 months) are as follows: from 28×60 to 11×60 s; from 15×60 to 7×60 s; from 10×60 to 3×60 s.

3.6.2 Change of melting temperature

Particular attention is paid in the production of thermostable fillings to the melting point, the temperature at which the product melts. It largely depends on the formulation components (together, the formulation components can both increase and decrease this temperature), in particular on their ability to form strong intermolecular interactions [93; 237 ; 274; 284; 288].

In Fig. 3.16 shows the change in the melting point of TF samples with different formulations, which were stored under different conditions.



a) b)

Fig. 3.16. Dependence of the TF melting point on the duration of storage at temperature: a) 2±2°C; b) –18±2°C; 1 – TF control sample; 2 – developed TF sample with sesame seeds concentrate

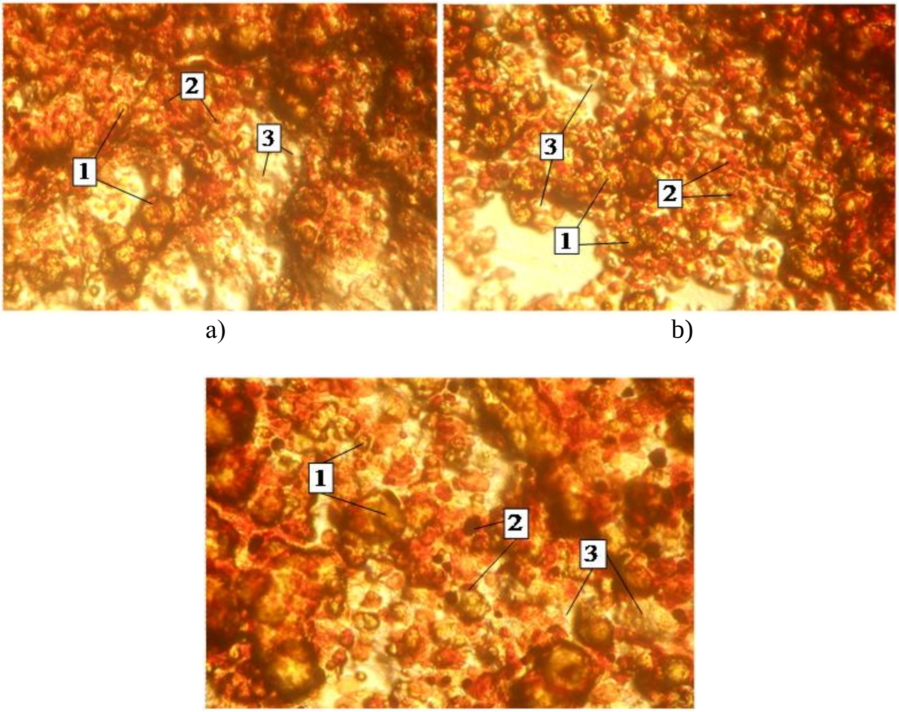
The above data (Fig. 3.16) show that during storage under different conditions for both TF (samples of TF with and without sesame seed concentrate), a decrease in melting point is observed. And freezing helps to reduce the melting point (there is a "loosening" of the structure due to the breakdown of bonds of different nature).

During the comparison of the melting point parameters of the studied samples, an increase in the melting point values in TF with a plant protein additive - a sesame seed concentrate, was recorded. This positive effect of sesame seeds concentrate on the melting point of the filling is due to the uniform distribution of moisture in the structure of the product, which during freezing causes slight damage to the structure [16; 31; 67; 135; 220].

After analyzing the results of both studies on changes in thermal stability and melting point, we can conclude. First, the long-term storage of the filling in two different conditions contributes to the reduction of thermal stability and melting point. This, as noted above, is mainly due to a decrease in moisture-holding ability and loss of moisture (syneresis).Secondly, the presence of sesame seed concentrate in the filling recipe composition has a positive effect on the technological properties of the product due to the formation of different forms of moisture bond: there is an increase in thermal resistance and melting point in products with the plant protein supplement. Thirdly, the freezing, due to the destruction of the skeleton filling with ice crystals, slightly reduces the technological characteristics of the product in accordance with the above trends.

3.7 Microstructure research of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

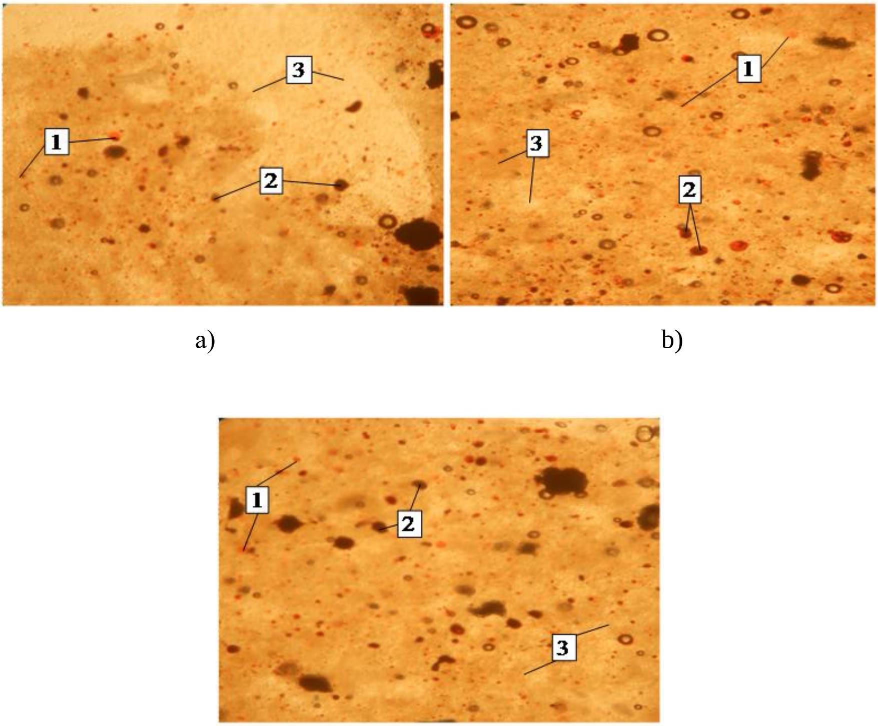
It is found that in the process of production of thermostable filling the recipe components undergo physical and chemical transformations. They combine different connections in a common spatial grid of pectin and starch to form a homogeneous structure. These interactions are capable of breaking or forming new bonds, primarily during storage, which leads to a change in the microstructure of the finished product.In Fig. 4.17 in order to clearly demonstrate these changes, a comparative characteristic of the microstructure of the following control samples is shown: a freshly made control sample, a control sample for which a rational shelf life at 2±2°C (15 days) and a control sample after its storage in a frozen state for 4 months (rational frozen storage conditions). In Fig. 3.18 shows the microstructures of samples of TF with sesame seed concentrate stored under the above conditions.



a) b)

c)

Fig. 3.17. Microstructure: a) control freshly made TF sample, b) control TF sample after 15 days of storage at 2±2°C, c) control TF sample after 4 months of storage at temperature –18±2°C with an increase of 120 times;1 - fat globules; 2 - grains of modified corn starch; 3 - pectin-sugar-milk base



a) b)

c)

Fig. 3.18. Microstructure: a) control freshly made TF sample with SSC, b) control TF sample with SSC after 15 days of storage at 2±2°C, c) control TF sample with SSC after 4 months of storage at temperature –18±2°C with an increase of 120 times;1 - fat globules; 2 - grains of modified corn starch; 3 - pectin-sugar-milk base

On the presented micrographs of fig. 3.17 and 3.18 show that the structure of the experimental samples looks like a spatial grid. The results of the study indicate the presence and uniformity of distribution of fat globules, which are an integral part of the sesame seeds concentrate and refined sunflower oil deodorized. The particle size of the sesame seed concentrate is about 50 μm, and the diameter of the fat globules is about 20… 60 μm

When comparing the micrographs, a slight difference in the microstructure of the test samples of TF and TF with the sesame seed concentrate was detected. In particular, due to the interaction of each composite component of the TF samples with the sesame seed concentrate, it is difficult to visually divide the boundaries of the structural elements, which indicates that they are ambiguity (Fig. 3.18).

Both test TF samples after 15 days of storage are more pronounced in the visibility of the constituent particles, in particular, fat globules and grains of corn modified starch contained in the starch paste are clearly visible. After all, as it is known during storage in the starch paste, a process of retrogradation (aging) takes place, during which its physicochemical properties (MHA and AHF) decrease. Thus, during the storage for 15 days, the structure of the TF samples is slightly compacted, indicating a slight weakening and change of connections[16; 31; 67; 135; 220].

The most clearly expressed are the constituent recipe components, in particular fat globules and starch grains, in the control TF sample and TF with sesame seeds concentrate, which have undergone low temperature storage, compared with freshly made samples. In addition, changes in pectin-sugar-milk basis before and after low-temperature storage of TF are not observed. This is likely to indicate a loss of strength and partial destruction of the bonds of a different nature between the TF prescription components during defrosting.

Thus, the results of the research show that the combination in thermostable filling of plant and dairy components causes the formation of different bonds, concentrated in a common pectin-starch mesh, which determines the properties of the framework and the homogeneous structure of the filling.

3.8 IR spectroscopic analysis of thermostable filling using dairy raw material and sesame seeds concentrate during storage under traditional conditions and frozen

In order to detect influence of the recipe components of the protein-polysaccharide nature in the case of their joint use in TF technology, spectra of filling absorption revealed during IR spectroscopy were studied. With this analysis, you can detect the presence of certain bonds between the component molecules and identify the substances that participate in this. The characteristic absorption bands of TF control and TF with

SSC are shown in Fig. 3.19, and their values and correspondence to certain functional groups are given in Table 3.17.

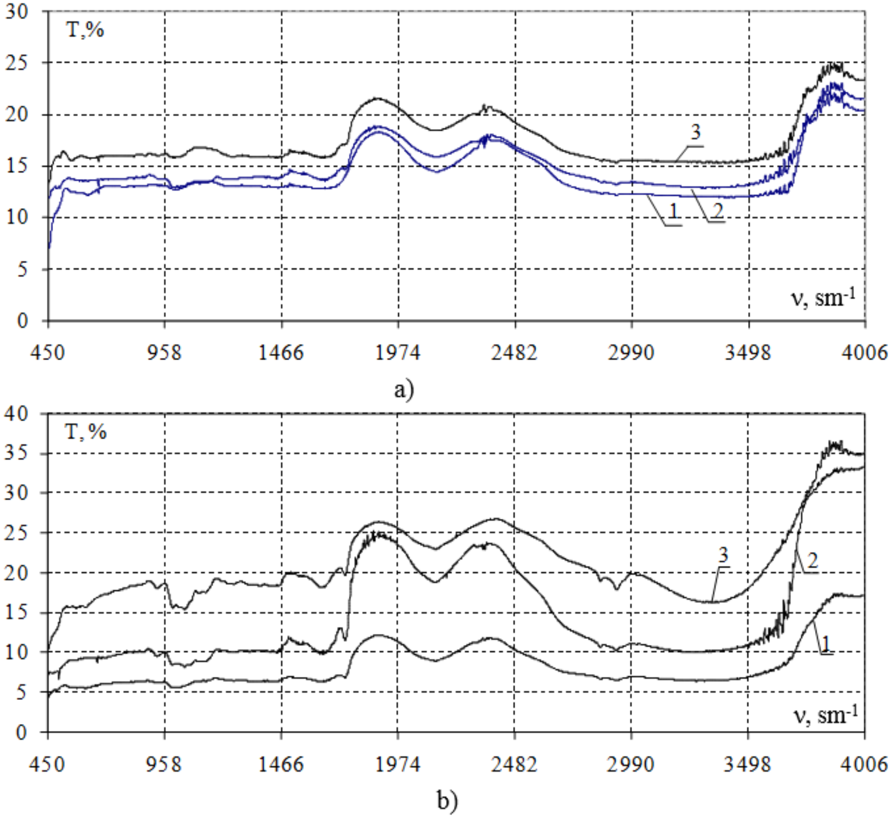


Fig. 3.19. IR spectra: a) control TF; b) TF with SSC; 1 - freshly made sample; 2 - sample after 15 days of storage at 2±2 °C; 3 - sample after 4 months of storage at –18±2 °C

Table 3.17

Characterization of absorption bands of IR spectra TF

Spectrum range, cm^{-1}					
3600…3100	3350…2850, 1100…900	2440…2350	2140…2100	1750…1720	550…450
OH-	CH-	C≡C	PH-	C=O	S=S

The spectra of all TF samples show wide absorption bands due to the valence vibrations of the bond of the functional group OH- (ν = 3600… 3100 cm^{-1}), which is involved in the construction of hydrogen bonds, that is, this group is characteristic of the recipe components of hydrophilic properties (sesame seed concentrate, skimmed milk powder, modified corn starch and low-esterified citrus pectin).These samples show absorption bands inherent in the deformation vibrations of the bond CH- group (3350…2850 and 1100…900 cm^{-1}), indicating the regrouping of intermolecular and intramolecular bonds, and the bands in the absorption region 2440…2350 cm^{-1} are characteristic of the valence vibrations of the C≡C group involved in the construction of alkenes. Therefore, these bands in the areas of absorption contribute to the rearrangement and the emergence of new interactions of the recipe components. Thus, these areas characterize the formation of a spatial grid of pectin and starch.

The absorption of bands in the region 2140…2100 cm^{-1}, caused by the fluctuation of organophosphorus groups RN-, is characteristic of skimmed milk powder and sesame seed concentrate. Which, in turn, probably indicates the interaction calcium of skimmed milk powder and calcium citrate with pectin molecules to form calcium bridges. The absorption bands detected in the TF samples in the range 1750…1720 and 550…450 cm^{-1} are characteristic of vibrations of the C=O and S=S groups, respectively, indicating the presence of low-molecular substances (fats, proteins, etc.) involved in the construction of high-molecular substances. (polysaccharides, etc.).

Thus, according to the results of the IR spectra, it is found that the components introduced into the TF formulation form constituents of chemical bonds of different nature, characterized by certain absorption bands. The result TH is formed with a common spatial grid of pectin and starch, which holds all the constituent components together.

3.9 Protein composition study of thermostable filling using dairy raw material and sesame seeds concentrate

It is known that the biological value of TF depends primarily on the content and properties of the protein, so the protein composition of control TF and developed TF with sesame seed concentrate was investigated. The bands of protein intensities and the spectra of their presence in TF are shown in Fig. 3.20.

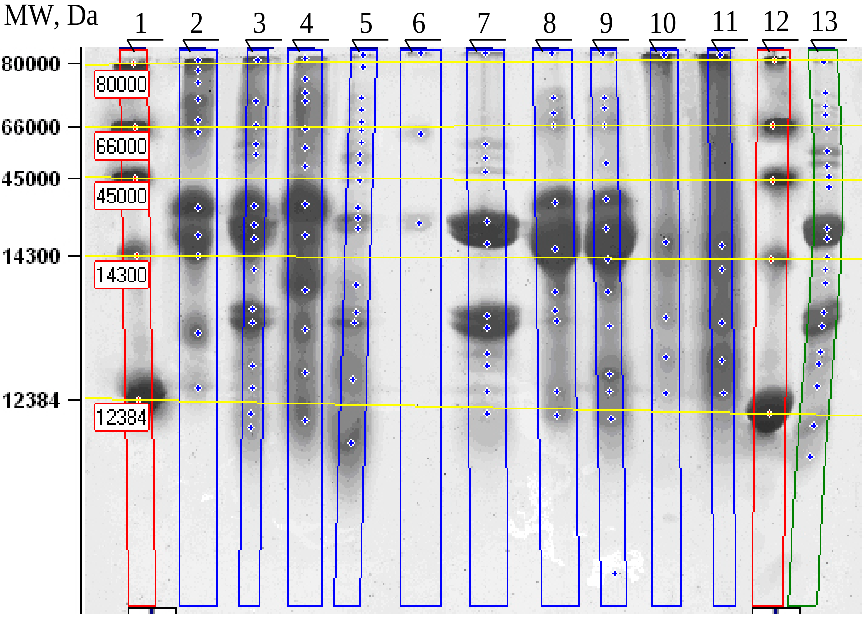


Fig. 3.20 Electrophoretic separation of proteins of control TF: 1, 12 - standards; 2 - total protein; 4 - water-soluble proteins; 6 - salt-soluble proteins; 8 - alcohol-soluble proteins; 10 - alkali-soluble proteins and developed TF with sesame seeds concentrate: 3 - total protein; 5 - water-soluble proteins; 7 - salt-soluble proteins; 9 - alcohol-soluble proteins; 11 - alkali-soluble proteins; 13 - the total protein of sesame seeds

From Fig. 3.20 found that the most significant peaks of the total protein of sesame seeds are peaks with a Molecular Weight (MW) of 26.4-22.6 and 13.48-13.8 kDa. These peaks correspond to proteins such as kaleosin and oleosin, which are characteristic of sesame seeds. However, some scientists claim that oleosin fractions are more diverse and may also have MW spectrum in the range of 12-20 kDa[240; 259].

From the presented data, it was found that the total protein of the control TF sample was divided into 11 bands, where the value of MW can identify the following proteins: 12.6 kDa - χ-casein; 14.2 kDa - lacto albumin; 20.6 kDa - λ-casein; 67.6 kDa - casein tetramer. In turn, the total protein of the developed sample with the sesame seed concentrate was divided into 15 strips; of these, 5 peaks coincide with the total protein of the control TF sample , and 7 have a close MW value to the sum of sesame protein. Also the MW peaks of 12.08 kDa, 14.08 kDa, 58.96 kDa, 66.27 kDa are unique. They are only fixed in the mixture, which may indicate the formation of strong covalent bonds between proteins in the developed TF sample and extract of sesame

In electrophoresis, water-soluble proteins have different separation spectra. The total amount of water-soluble proteins for the control and developed sample is 25.75 and 28.09 mg protein /1 g of product, respectively. In water-soluble proteins of the developed TF sample revealed residual amounts of oleosin and kaleosin, which were introduced by the addition of sesame in the product. Also, fractions of 44.45 MW-54.4 kDa water-soluble proteins coincide in motility with bands of sesame protein in the same mass range.It should be noted that in this sample of proteins, bands with a molecular weight of 76.4, 73.29, 57.3, 21.2, 12.17 kDa are disappear, which were in the separation spectrum of the control TF sample. However, in this TF sample, the occurrence of new water-soluble proteins is recorded, in particular new bands appear with MW 79.09; 59.3; 28.67 kDa, which are probably the products of joint interaction of proteins of dairy and plant origin, since these bands are not detected in either the control or the total sesame protein.

From the analysis of the fractional composition it was found that the total amount of salt-soluble proteins of the control TF sample is 3.75 mg of protein/1 g of product, and developed - 29.26 mg of protein/1 g of product. Electrophoresis of the isolated salt-soluble proteins of the control sample showed that the starting material contained very little protein material. It was divided into only 3 strips. However, in the salt soluble proteins of the developed TF sample revealed bands of oleosin and kaleosin, which were introduced by the addition of sesame. It should also be noted that in the process of proteins separation of the salt-soluble fraction of the developed TF sample identified 12 strips. They also contain new protein strips with MW 59.09 and 12.31 kDa. In the proteins of this sample, bands with a molecular weight of 63.03, 26.11 kDa are disappear, which were in the separation spectrum of the control TF sample.

The total amount of alcohol-soluble proteins of the control and developed samples of TF are 12.29 and 7.61 mg of protein /1 g of product, respectively . These proteins were divided into 11 and 14 strips, respectively. In this case, alcohol-soluble proteins isolated from the developed TF sample do not have strips with MW 68.89, 17.19 and 13.62 kDa, which were detected in the protein separation spectrum of the control TF sample. As in the previous proteins, in these proteins in the developed TF sample there are new strips with MW 25,97; 10.32 kDa.

Alkaline extraction showed that the total amount for the control sample is 42.13 mg of protein /1 g of product, and for the developed TF sample - 40,96 mg of protein /1 g of product. Proteins isolated from both samples are found to be heterogeneous and consist of polypeptides with large variations of molecular weight spectrum values. Because of this, there is a significant peptide background. In the alkaline-soluble fraction of the control and developed sample of TF also allocated 6 and 7 strips of proteins, respectively. Significant background coloring is observed, which complicates the evaluation of the MW of the divided strips. From the received data it can be noted that in the developed TF sample compared with the control, proteins with MW 13,56 and 13,07 kDa were not detected.

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