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# THE EFFECT OF MONO- AND DISACCHARIDES ON STRUCTURAL-MECHANICAL PROPERTIES OF PECTIN GELS

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*Вивчено вплив глюкози, фруктози, сахарози і лактулози на структурно-механічні та тиксотропні властивості пектинового гелю в яблучному пюре. Проведено порівняльний аналіз участі моно- і дисахаридів у формуванні пектинового гелю. Визначено втрати пребіотикалактулози при зберіганні гелів. Розраховано раціональні співвідношення яблучного пюре і цукрів для формування рецептур кондитерських виробів функціонального призначення*

*Ключові слова: пектинові гелі, глюкоза, фруктоза, пребіотиклактулоза, тиксотропія, тиксотропні властивості, функціональні продукти, яблучне пюре*

*Изучено влияние глюкозы, фруктозы, сахарозы и лактулозы на структурно-механические и тиксотропные свойства пектинового геля в яблочном пюре. Проведен сравнительный анализ участия моно- и дисахаридов в формировании пектинового геля. Определены потери пребиотикалактулозы при хранении гелей. Рассчитаны рациональные соотношения яблочного пюре и сахаров для формирования рецептур кондитерских изделий функционального назначения*

*Ключевые слова: пектиновые гели, глюкоза, фруктоза, пребиотиклактулоза, тиксотропия, тиксотропные свойства, функциональные продукты, яблочное пюре*

## 1. Introduction

Technologies of many confectionery products (marmalade, gel-like structure candies, fillings for caramel, pastry, muffins, honey-cakes, cakes) are based on the gelation of pectin substances of apple puree. Availability of sugars is the influential component of mechanism of the gelation of pectin. They serve not only as the carrier of sweet taste but also contribute to the desolvation of pectin molecules, the result of which is their association with each other.

Traditional technologies imply the use of disaccharide saccharose and there are practically no designs in relation to the formation of pectin gels on other sugars, including monosaccharides – glucose, fructose, disaccharide lactulose. In this case it is known that glucose is expedient to use for creating the assortment of products for children, fructose – in the technologies of products for patients with diabetes mellitus, lactulose is recommended to use in the development of production with functional properties. A change in the nature of sugars will have an essential effect on the behavior of pectin substances of apple puree in the process of gelation, on the formation of structural and mechanical properties of the finished products. Therefore, the represented studies of the process of gelation of pectin substances of apple puree in the presence of glucose, fructose and lactulose are relevant. Another important question is the study of thixotropic properties of the obtained gels, when there is a production necessity for destruction of prematurely formed grid of gel for the molding of confectionery products.

Of significant interest are the studies of preservation of the prebiotic lactulose in the process of storing pectin gels on mono- and disaccharides. Obtained data must be taken into account when designing confectionery production with functional purpose.

## 2. Literature review and problem statement

Pectin substances form gel-like consistency of many foodstuffs, especially confectionery products. The structure of pectin is predetermined by galacturonic acid (GaLA) and according to the classification of FAO and the European Union, the product with the name "pectin" must contain not less than 65 % – fragments of GaLA [1, 2]. The fragments of galacturonic acid can be methylesterified. The degree of esterification of pectin classifies them as high-methoxylated (H-pectins) and low methaxylated (L-pectins). The degree of esterification (DE) of high-methoxylated pectins must exceed 50 %. Different types of pectins are standardized according to commercial application. High-methoxylated pectins are standardized according to the unified gelling ability of pectin, particularly by the amount of sugar necessary for the formation of gel of 1 kg of pectin. The majority of high-methoxylated pectins are marked to 150, i. e., for the gel formation of 1 kg of pectin, it is necessary to have up to 150 kg of saccharose at pH=2,2–2,4 and the content of dry substances 65 % [2]. We examined conditions of the gel formation based on high-methoxylated pectin contained in apple puree.

For manufacturing apple puree, which is widely used by confectionery industry, they use, as a rule, apples with expressed taste and flavour, not a bright color range, at the stage of “waxy” ripeness. In this period they accumulate the largest amount of pectin (0,9...1,1 %), which creates the structure of a finished product.

Molecules of pectin are dispersed in the dispersion medium and under the action of heat are found in the state of constant motion. Because of the presence in their composition of dissociated carboxyl groups, they possess negative charge of high density [3, 4] and are repulsed from each other, without forming gel grid. For successful formation of gel structure, the necessary conditions are availability of acids and saccharose. Acid, as more dissociated than pectin, decreases the electric charge of its molecules. Therefore, when using apple puree as the base for the gelled confectionery products, its acidity must comprise 0,9...1,0 % of malic acid. Another necessary condition for forming pectin gels is the presence of dehydrating component, whose role in the food gels, as a rule, is performed by saccharose. Under its influence, bare sections of pectin molecules appear [5], which are connected by means of homopolar, heteropolar and associated bonds, Fig. 1.

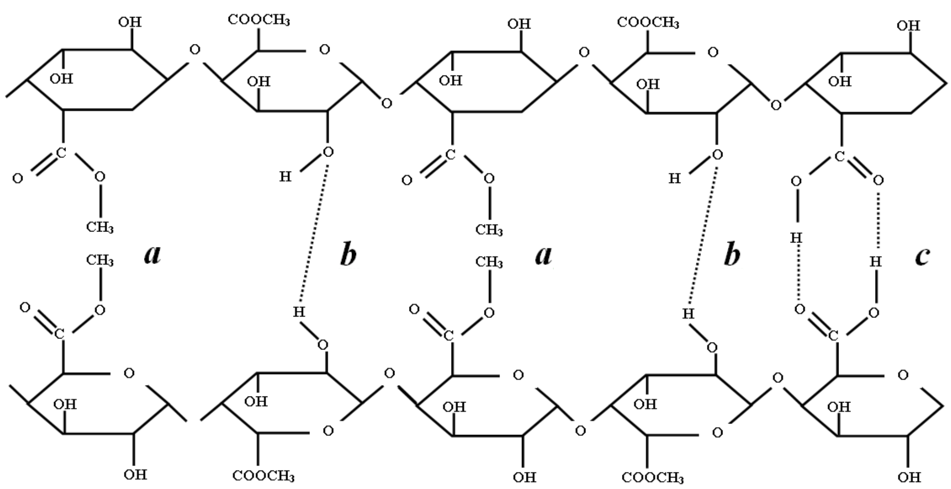



Fig. 1. Mechanism of gel formation of H-pectin: *a* — hydrophobic interaction; *b* — hydrogen bonds of hydroxyl groups; *c* — hydrogen bonds of carboxyl groups

Marmalade, candies of gelled structure, fillings for caramel, pastries, muffins, cakes, honey cakes are the products, in which the carrier of sweet taste is predominantly saccharose. The formation of pectin gels with the disaccharide saccharose is sufficiently studied. Papers [6, 7] point to the important role of hydroxyl groups of saccharose in the process of gel formation of pectin and stabilization of the binding zones of pectin molecules by saccharose. Scientific knowledge naturally affected the market for saccharine confectionery products. Review of assortment of products on pectin with the gelled structure [8–12] testifies to the prevalence of products with the use of saccharose.

However, under contemporary conditions, the products with fructose, glucose, lactulose and other sugars start to take their important place. But in this case, there is no sufficient scientific information about the formation of pectin gels with various mono- and disaccharides, including pectin gels with the monosaccharides glucose, fructose, etc. This does not make it possible to form uniform opinion about the patterns of influence of different sugars on the gel formation of pectin molecules and inhibits development of sector of confectionery products for children, dietetic and functional food.

For example, article [13] presents data on rheological properties of gels of high-methoxylated pectin, formed with different sugars (saccharose, glucose, and fructose). They testify that the consistency, viscosity and fluidity of gel systems increase in the following order: saccharose, glucose, fructose. The values of dynamic modulus of elasticity grow in analogous order for the examined samples, which indicates the formation of stronger gels in monosaccharides, especially so with fructose.

At the same time, authors [14–17], in the course of studying questions of the use of fructose in the production of diabetic pastila-marmalade products, noted opposite data. It was established that the strength of zephyr and marmalade mass on fructose, as well as the values of their critical shear stress, are substantially less than the control samples on saccharose. This was the reason to increase formulation amount of pectin and to increase the content of dry substances in confectionery mass. Authors [16, 17] offered explanation about fructose, as monosaccharide, being capable of retaining a smaller amount of water than saccharose and, therefore, it reduces its polarity to a lower degree, which does not contribute to aggregation of hydrophilic molecules of pectin and to the formation of gel. With the purpose of strengthening the structure of marmalade on pectin and fructose, authors [18] recommend using fructose in combination with lactitol in equal ratio.

Papers [19, 20] explored the influence of varieties of sugars on the temperature of gel formation of high-methoxylated pectin and found that the replacement of saccharose with glucose and fructose causes large drops in the temperature of gel formation. In the presence of fructose, the temperature of gel formation substantially reduces while in the presence of glucose, on the contrary, the temperature of gel formation rises. In this case, data on structural and mechanical properties of the formed gels are lacking.

Authors [21] present results of studying the formation of gel of low methaxylated amidated pectin and sugars (saccharose, glucose, fructose). In the studies they established the absence of correlation between the adsorption of water by sugar and gel rigidity. The influence of different sugars is explained by competition between sugar and pectin for the cations of calcium. However, obtained data cannot be used for high-methoxylated pectin since the mechanism of formation of their gel is different from the mechanism of formation of gel of low methaxylated amidated pectin.

Thus we did not find comprehensive studies that would make it possible to establish the patterns of influence of different mono- and disaccharides on the formation of structural and mechanical properties of gel of high-methoxylated pectin. In this case, structural and mechanical properties in particular will form the consistency of finished product and affect the course of technological process. The properties of glucose, lactulose and fructose differ significantly from the properties of saccharose, which necessitates conducting the complex of studies, devoted to determining the influence of glucose and fructose on structural and mechanical properties of pectin gels. This will help to design scientifically substantiated technologies of pectin gels, which may be used in manufacturing products for children (with glucose), functional products (with lactulose) and dietetic products for patients with diabetes mellitus (with fructose), the glycemic index of which is 20 %, and that of saccharose is 68 %.

At present, considerable attention in the world is paid to the development of functional products. The term "functional food product" was proposed in Japan in 1984 in the national scientific project "Systematic analysis and development of the functions of food products", which was introduced by the Ministry of Education, Science and Culture [22]. Legislatively, this term was adopted in Japan in 1991 when implementing the system Foshu (FoodforSpecifiedHealthUse), in which it was indicated that functional food products are natural or prepared foodstuffs that contribute to physiological activity of the human organism, protect from the threat of infectious diseases. According to the concept [23, 24], the Japanese Ministry of Health and Social Welfare included in the functional food products:

– foodstuffs, which have certain positive effect on human health and which do not contain allergens;

– food products, in which there is a scientifically substantiated positive effect on physiological functions of organism.

Shortly afterwards, in connection with the growing interest, the European Union formed the European Commission for actions within the framework of "the science on the functional food" in Europe (FUFOSE). The task of this commission was development and approval of scientifically substantiated approach to activities, necessary for support of development of production of foodstuffs, which can exert therapeutic influence on certain physiological functions, as well as may improve health and/or decrease the risk of diseases [25].

In different countries of the world characteristics of a "functional food product" differ; however, they all attest to the fact that the foodstuff with a "functional" status must render certain positive effect on human health.

The most appropriate characteristic of a functional food product is represented in the terminological GOST R 5234902005 "The food products. The functional food products". According to this standard, a "functional product" is the food product, intended for systematic use in the composition of food rations by all ages of healthy population, which preserves and improves health due to the presence in its composition of physiological-functional ingredients. Physiological-functional food ingredients are the natural substances or a complex of substances of animal, plant, microbiological, mineral origin, or identical to natural, as well as living microorganisms, which are included in the composition of the functional food product. They possess the capacity to favorably affect one or several physiological functions, the process of exchange of substances in the human organism at their systematic consumption in the amount of 10 to 50 % of the daily consumption. The group of physiological-functional food ingredients includes: vitamins, mineral substances, prebiotics, probiotics, simbiotics, essential amino acids, polyunsaturated fatty acids, cross-linked starches, vegetable fibers.

Such a physiological-functional food product is prebiotic lactulose, acknowledged as one of the best prebiotics in the world. In Japan, lactulose is included in the strategic products for maintaining health of the nation. Lactulose is the disaccharide, which consists of the molecules of fructose and galactose. It possesses the following properties: caloric content – 16,75 kJ/g (4,0 kCal/g), solubility is 75,2 %, melting point is 442 K (169,0 °C), sweetness is 0,50 un., glycemic index is 46 %. The basic properties of lactulose as a prebiotic, consist in the fact that it normalizes the work of digestive system. Lactulose reaches thick bowels, where it becomes food substrate for for bifidus and lactobacillus. Lactulose suppresses the action of pathogenic microflora.

At present, lactulose is widely used in the production of dairy products and products for baby food. When conducting analysis of literary sources, we did not find information on the application of lactulose in the production of pectin gels and about the influence of the disaccharide lactulose on structural and mechanical properties of pectin gels, prepared on saccharose, fructose or glucose. Therefore, a promising task appears to be the study of structural and mechanical properties of pectin gels, prepared on the mixtures of sugars: saccharose-lactulose, glucose-lactulose, fructose-lactulose. Obtained data may be used for designing confectionery products with the gelled structure (marmalade, candies, fillings) with the "functional food product" status.

## 3. Aims and objectives of the research

The aim of this work is study and comparative analysis of the formation of structural and mechanical properties of pectin gels on apple puree with glucose, fructose, saccharose, lactulose for using the data in the technologies of confectionery products.

To achieve the set aim, the following tasks were formulated:

– to establish rational ratios for the gel formation of apple puree with glucose, fructose, saccharose and to determine structural and mechanical properties of pectin gels;

– to substantiate rational amount of lactulose in pectin gels and to explore its influence on rheological and thixotropic properties of gel;

– to determine the losses of lactulose in the process of production and storing pectin gel on apple puree with saccharose, fructose, glucose for calculating the formulation compositions of confectionery products with functional properties.

## 4. Materials and methods of research

Research into the influence of disaccharides (saccharose, lactulose) and monosaccharides (glucose, fructose) on the properties of pectin gels were conducted on the samples: "apple puree – carbohydrate". Apple puree was obtained from the apples "Antonovka" and had the following physical chemical indicators: the content of dry substances – 10 %, of saccharose – 1,3 %, of reducing substances – 7,5 %, acidity (in conversion to malic acid – 0,8 %), the content of pectin – 0,9 %.

We used as carbohydrates: white crystalline sugar with the content of dry substances – 99,85 %; glucose – with the content of dry substances 91 %; fructose – with the content of dry substances 98 %, lactulose with the content of dry substances 99,9 %.

One can familiarize with the methods of experimental study in paper [26].

## 5. Results of studies of the influence of glucose, fructose, saccharose, lactulose on the structural and mechanical properties of pectin gels on the apple puree

In the majority of formulations of confectionery products of the gelled structure, the ratio of apple puree and carbohydrates comprises 1,3:1,0, which was used as the basis for the examined formulation compositions. The amount of carbohydrates (saccharose, glucose, fructose) is calculated according to the equal amount of dry substances. The examined samples were represented as follows:

– 130 g of apple puree (10 % of dry substances) + 100 g of saccharose (99,85 g of dry substances);

– 130 g of apple puree + 109,72 g of glucose (99,85 g of dry substances);

– 130 g of apple puree + 101, 89 g of fructose (99,85 g of dry substances).

Moisture content of the three samples comprised, respectively, 51,0; 52,93; 51,34 %. All three samples were exposed to boiling to reaching 70 % of dry substances, which corresponded to the moisture content of 30 %. The boiled masses, which corresponded to the state of sol, were cooled to the temperature of 293 K (20 °C). The cooling process was accompanied by the transfer of sol to the state of gel. Since the structure of pectin gel develops over time, the samples were kept to cure for 120 minutes and only then we determined their structural and mechanical characteristics. Fig. 2, *a–c* demonstrates results of the studies on determining the dependence of effective viscosity ($\eta_{ef}$) on the shearing rate in the range from 2,45 to 1073 $s^{-1}$ (destruction of structure to the state of sol) and in the range from 1073,00 to 2,45 $s^{-1}$ (restoration of structure to the state of pectin gel): based on apple puree – saccharose (a), – fructose (b), – glucose (c).

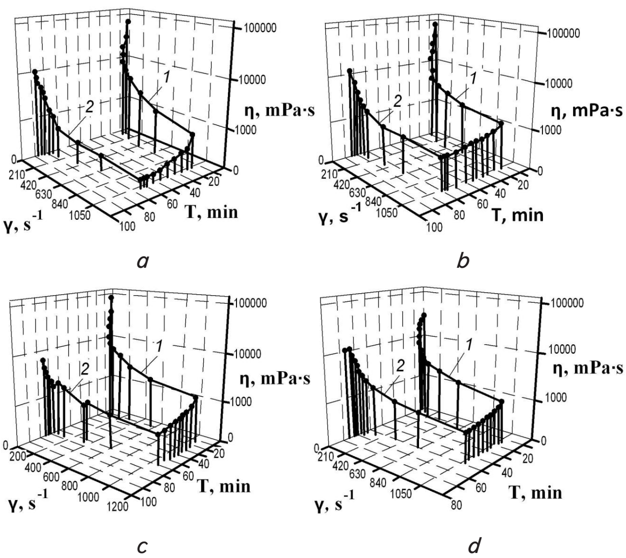



Fig. 2. Rheological curves of pectin gel based on: *a* — apple puree and saccharose; *b* — apple puree and fructose; *c* — apple puree and glucose; *d* — apple puree and glucose with the decrease in its amount

Table 1 presents rheological characteristics of pectin gels.

Results of data analysis of Table 1 demonstrate that the viscosity of pectin gel on glucose and fructose is 1,3 times larger than the viscosity of pectin gel on saccharose. The role of saccharose, glucose, and fructose consists both in the reduction of solvation of structural pectin body, which contributes to the cohesion of separate particles along the desolvated sections, and in the occurrence of hydrogen bonds between the molecules of sugars and the dehydrated molecules of pectin. Saccharose, glucose, fructose were introduced into the composition of pectin gel in the amounts of equal by mass dry substances. However, the number of molecules of glucose and fructose will be 1,9 times larger than the molecules of saccharose (molecular weight of saccharose – 342, glucose and fructose – 180). That is why in the pectin gels based on glucose and fructose, hydrogen bonds with the molecules of pectin are formed in a larger amount. This contributes to strengthening the structure of pectin gels on glucose and fructose.

Table 1

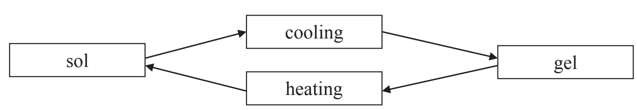
Rheological characteristics of pectin gels

| Pectin gel on | $\eta_{ef}^{0}$, Pa·s | $\eta_{ef}^{b}$, Pa·s | $\eta_{ef}^{r}$, Pa·s | $\lambda_t$, % |
|---|---|---|---|---|
| saccharose | 47,1±1,5 | 0,9±0,1 | 8,5±0,5 | 18,0 |
| glucose | 62,5±1,5 | 1,05±0,1 | 13,5±0,5 | 21,6 |
| fructose | 61,3±1,5 | 1,1±0,1 | 13,3±0,5 | 21,7 |
| gel on glucose with the decrease in its amount by 30 % | 49,34±1,5 | 1,09±0,1 | 12,67±0,5 | 25,7 |

However, these bonds are weak and under the action of mechanical action they are destroyed. At the shearing rate of 1076 $s^{-1}$, there occurs complete destruction of the structure. Coefficient of thixotropy (Table 1) is 18...22 %, which, according to classification [27–34], corresponds to the mark "unsatisfactory".

Under manufacturing conditions, a premature process of the sol passing into gel sometimes occurs. The formed gel does not make it possible to mould the products of specific form (marmalade, jujube, candies). For the formation of the specified confectionery masses, their structure must be in the form of sol.

Temperature significantly influences the state of pectin structure. During cooling the pectin sol passes into gel; at heating, gel passes into sol according to the following scheme:




If the premature (before the process of molding) transfer of sol into gel occurred, then the increase in temperature will contribute to the reverse passage of gel into sol. However, the action of high temperature (higher than 348 K (75 °C)) will contribute, at repeated transfer of sol into gel, to the weakening of the structure of gel due to acid hydrolysis of pectin molecules to pectin or pectin acids. Therefore, a more expedient transition mode of gel into sol is the method of mechanical action, i.e., thixotropy. Article [28] for the first time indicated the possibility of converting gel into sol with the help of mechanical processing at constant temperature.

In the production they frequently use the transition mode of gel into sol at slight mechanical load – 3...5 $s^{-1}$. The structure destroyed in such a way to the state of sol allows conducting the process of molding. The conducted studies made it possible to determine the coefficient of thixotropy of the restored structure – $\lambda_m$ =85...90 %, which corresponds to the mark "excellent" and characterizes it as practically not weakened.

The transfer of pectin sol into gel is accompanied by packing of the structure, which subsequently continues to be condensed. Table 2 displays results of research into the strength of structure of pectin gel on saccharose, glucose and fructose in the process of curing.

Table 2

Influence of duration of curing of pectin gel on the value of its strength

| Pectin gel with | Strength of pectin gel at temperature of 293 K (20 °C), g | | | | |
|---|---|---|---|---|---|
| | 2 hours | 6 hours | 10 hours | 24 hours | 36 hours |
| saccharose | 322,0 | 350,2 | 385,4 | 396,8 | 405,6 |
| fructose | 393,7 | 443,1 | 474,1 | 480,5 | 482,5 |
| glucose | 483,5 | 523,9 | 576,3* | 584,5** | 599,3*** |

*Note: * – occurrence of crystals of glucose; ** – sufficient amount of crystals of glucose; *** – crystallization of glucose throughout the entire volume of pectin gel*

It was found that the structure of all samples is strengthened; however, in 10 hours of curing, the sample on glucose revealed crystallization of glucose, which in the process of curing is intensified, and after 36 hours of curing, the pectin gel transformed to the crystallization structure.

The reason for crystallization of glucose during curing of pectin gel is low solubility of glucose (Table 3).

Table 3

Solubility of glucose, fructose, saccharose depending on temperature

| Sugars | Solubility, % depending on temperature K/°C | | | | | |
|---|---|---|---|---|---|---|
| | 293/20 | 303/30 | 313/40 | 323/50 | 333/60 | 343/70 |
| Saccharose | 67,09 | 68,70 | 70,42 | 72,25 | 74,18 | 76,22 |
| Glucose | 47,72 | 54,64 | 61,83 | 70,91 | 74,73 | 78,23 |
| Fructose | 78,94 | 81,64 | 84,34 | 86,10 | 89,30 | – |
| Lactulose | 75,20 | 76,40 | 77,60 | 79,80 | 81,50 | 86,00 |

Data demonstrate that the solubility of glucose at temperature of 293 K (20 °C) is 40 % lower than the solubility of saccharose and is 70 % lower than the solubility of fructose.

However, the solubility of sugars increases with the increase in temperature, and at temperature of 343 K (70 °C), which corresponds to the temperature of start of the process of gel formation, the solubility of glucose is 2 % larger than the solubility of saccharose. Glucose in the intermicellar dispersion medium at the specified temperature is in the dissolved state. In the course of cooling the system down to 313 K (40 °C), the solution of glucose gradually passes from unsaturated state to the saturated. At temperature of 293 K (20 °C), the solution of glucose in intermicellar dispersion medium converts to the supersaturated state, which is accompanied by the process of crystallization. The amount of crystals of glucose over time exponentially increases and in 24 hours pectin gel acquires coagulation-crystalline structure. In 36 hours, the crystallization of glucose occurs throughout the entire volume of pectin gel.

For preventing the crystallization of glucose in pectin gels, it is proposed to reduce its amount. The conducted studies revealed that the reduction in the amount of glucose by 30 % enabled reaching the values of effective viscosity of the undestroyed structure of pectin gel of the values of effective viscosity of gel on saccharose (Fig. 2, *d*). Viscosity value of the undestroyed, completely destroyed and restored structure of pectin gel with the reduced amount of glucose by 30 % is represented in Table 1.

Analysis of the obtained data demonstrated that the reduction in the amount of glucose by 30 % changed the ratio of apple puree and glucose from 1,3:1 to 1,7:1,0. Effective viscosity of the undestroyed structure of pectin gel was reduced from 62,5 to 49,34 Pa·S, i. e., by 1,27 times. The gel became more mobile, which is testified by the growth in coefficient of thixotropy – to 25,7 %.

In the production of pectin gels with the functional (health-improvement) properties, the decision was made that 100 g of pectin gel with the moisture content W=30 % on saccharose, glucose, fructose must provide for the daily norm of lactulose, which is 10 g. Lactulose was introduced into the composition of sol at the end of boiling at temperature of 378–383 K (105...110 °C). The formulation compositions of the examined samples are represented in Table 4.

Table 4

Formulation compositions of pectin gels with functional properties

| Name of component | Amount of component, g | | |
|---|---|---|---|
| | model 1 | model 2 | model 3 |
| Apple puree | 130,00 | 130,00 | 130,00 |
| Saccharose | 83,70 | – | – |
| Glucose | – | – | 64,96 |
| Fructose | – | 85,59 | – |
| Lactulose | 16,30 | 16,30 | 11,84 |
| Yield | 161,30 | 161,30 | 118,43 |

Table 5 presents rheological characteristics of the gels of models I, II, III: effective viscosity of the practically undestroyed and practically destroyed structure, coefficient of thixotropy.

Table 5

Rheological properties of gels with functional properties

| Model of gel | $\eta^0_{ef}$, Pa·s | $\eta^b_{ef}$, Pa·s | $\eta^r_{ef}$, Pa·s | $\lambda_t$, % |
|---|---|---|---|---|
| No. 1 Apple puree, saccharose, lactulose | 40,3 | 8,5 | 7,1 | 20,3 |
| No. 2 Apple puree, fructose, lactulose | 63,9 | 8,2 | 29,0 | 45,0 |
| No. 3 Apple puree, glucose, lactulose | 44,2 | 1,1 | 11,3 | 25,0 |

Analysis of the Table 5 data showed that lactulose in the composition of pectin gel on saccharose decreases effective viscosity of the undestroyed structure by 14,5 %, based on glucose – by 10,4 %, while that based on fructose is, on the contrary, increases the viscosity by 4,2 %. Such an influence of lactulose on the effective viscosity of gels is explained by differences in the solubility of the examined sugars. Thus, at 293 K (20 °C), the solubility of lactulose is 75,2 %, which is 12 % higher than the solubility of saccharose, 57 % higher than the solubility of glucose and 4 % lower than the solubility of fructose.

Rheological properties of gels with functional properties, represented in Table 5, attest to the fact that lactulose in the pectin gels on saccharose and glucose will contribute to the increase in free water in the structure of gels and, on the contrary, contribute to the decrease in the amount of free water in the gels on fructose. To confirm the given hypothesis, we performed differential thermal analysis of the examined samples. As a result of the analysis, the total losses of moisture by the samples are established at the increase in temperature, as well as the numerical ratio of free and bound moisture, Fig. 3.

It was conditionally accepted during the analysis that the moisture, which is released by the sample to the boiling point, may be considered free, and the moisture, which is released by the sample exceeding the boiling point, may be considered bound. Since the boiling point for the solutions of different sugars essentially differs and depends on their concentration, it was calculated that the boiling point of the examined samples of pectin gels must correspond to the 80 % solutions of sugars. Thus, in the studies we used pectin gels of humidity 30 %, which in the process of heating to 373 K (100 °C) lost ≈10 % of moisture, and their content of dry substances by this moment increased to ≈80 %. Taking into account data [33], the boiling point of the 80 % solutions of saccharose, glucose, fructose is 382,1 K (109,4 °C), 386 K (113 °C) and 397 K (124 °C), respectively. That is why the moisture on the curve TG was considered free until the moment of reaching by gel-sol on saccharose the temperature of 382,1 K (109,4 °C); by gel-sol on glucose – 386 K (113 °C); by gel-sol on fructose – 397 K (124 °C). Table 6 presents the analysis of results of derivatographic studies, which confirms the hypothesis, proposed as a result of conducted rheological research.

Table 6

Content of free and bound moisture of pectin gels on saccharose, glucose, fructose

| Pectin gel based on | Total amount of moisture, removed from the sample at heating, % | Content, % of the total amount | | Activation energy |
|---|---|---|---|---|
| | | free moisture | bound moisture | |
| Apple puree, saccharose | 31,80 | 44,00 | 56,00 | 26,30 |
| Apple puree, saccharose, lactulose | 34,00 | 45,40 | 54,60 | 28,92 |
| Apple puree, glucose (with the decrease in the amount by 30 %) | 20,80 | 42,00 | 58,00 | 19,71 |
| Apple puree, glucose (with the decrease in the amount by 30 %), lactulose | 26,10 | 44,00 | 56,00 | 30,83 |
| Apple puree, fructose | 40,40 | 58,00 | 42,00 | 67,14 |
| Apple puree, fructose, lactulose | 38,80 | 56,60 | 43,40 | 41,50 |

Actually, the replacement of 10 % of saccharose or glucose with lactulose contributes to the increase in the amount of free water and naturally increases the total amount of moisture, removed at heating. This is explained by the increase in general solubility of sugars in the system "pectin – saccharose – lactulose" and "pectin – glucose – lactulose" in comparison to the monocomponent solutions of saccharose or glucose. With the addition of the disaccharide lactulose, the overall cohesion of the system decreases.

For the gels on fructose, the addition of lactulose, on the contrary, increases the amount of bound water, in connection with which such systems release less moisture at heating. This is connected to the decrease in the index of solubility of sugars in the combination fructose – lactulose in comparison with the solutions on fructose.

Thus, when creating fruit gels on apple puree with functional properties, it is necessary to take into account that the disaccharide lactulose reduces the amount of bound moisture in the gels on saccharose and glucose, in connection with which the viscosity of gel-sol decreases. And vice versa, it increases the amount of bound moisture in the pectin gels on fructose, which correspondingly increases their viscosity. This will be reflected in the conditions of forming gel masses, their thixotropic properties.

Along with the study of influence of lactulose on structural and mechanical properties of gels, an important question is the study of preserving lactulose in the process of production, since the losses of prebiotic will necessitate the recalculation of its formulation amount and thus the influence of lactulose on the structure of gel systems may become more significant.

Table 7 presents results of the analysis of gas-liquid chromatography on determining preservation of lactulose in the production of pectin gels based on saccharose, fructose, and glucose when storing the gels for 7 days.

Table 7

Content of lactulose in pectin gels with functional properties

| Model of gel | Content of lactulose, g, in 100 g of pectin gel | | |
|---|---|---|---|
| | 0 days | 7 days | Losses, % |
| No. 1. Apple puree, saccharose, lactulose | 10,00 | 9,00 | 10,00 |
| No. 2. Apple puree, fructose, lactulose | 10,00 | 8,56 | 14,40 |
| No. 3. Apple puree, glucose (with the decrease in the amount by 30 %), lactulose | 10,00 | 8,82 | 11,80 |

According to data of Table 7, the content of lactulose in the process of storing pectin gels reduces. That is why the percentage of losses of prebiotic in gels on different forms of sugars must be taken into account when designing the formulations of confectionery products of functional designation.

Taking into account the losses of lactulose, we carried out correction of the rational ratio of formulation components of pectin gels on saccharose, fructose and glucose with functional properties, which are given in Table 8.

The formulation compositions of pectin gels represented in Table 8 are the basis for developing a broad line-up of confectionery products for mass, children, and dietetic food of functional designation. The products are not only a valuable source of the micro- and macroelements, vitamins, food fibers, pectin but are also capable of providing for the daily need of human organism in the prebiotic lactulose.

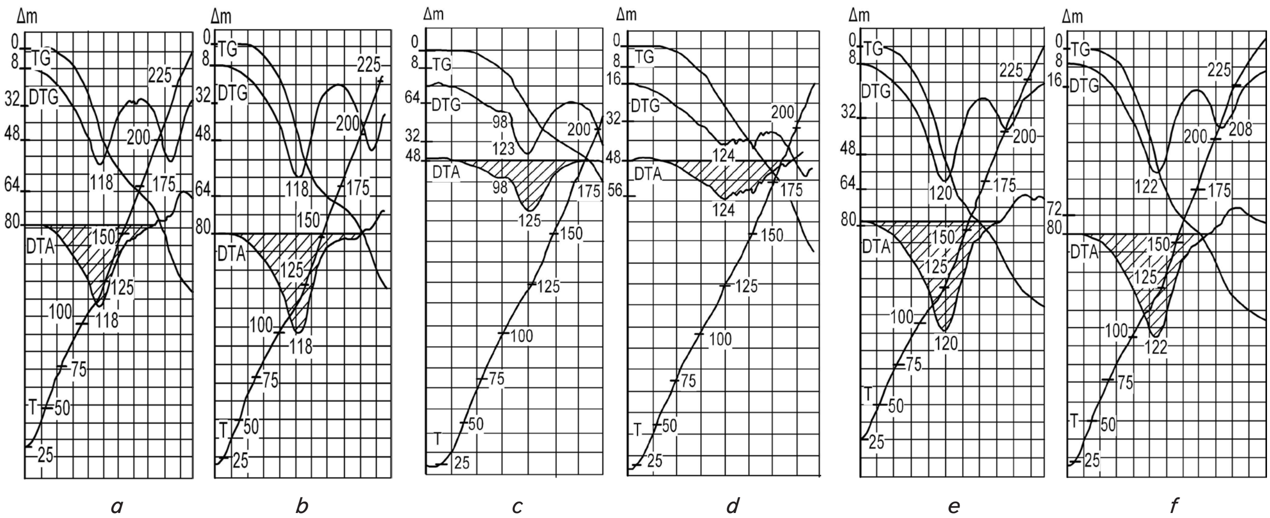


Fig. 3. Derivatograms of heating pectin gels: *a* — with saccharose; *b* — with saccharose and lactulose; *c* — with glucose (with the decrease in the amount by 30 %); *d* — with glucose (with the decrease in the amount by 30 %) and lactulose; *e* — with fructose; *f* — with fructose and lactulose

Table 8

Formulation compositions of pectin gels with functional properties

| Name of component | Amount of component, g | | |
|---|---|---|---|
| | model 1 | model 2 | model 3 |
| Apple puree | 79,79 | 79,44 | 108,49 |
| Saccharose | 51,37 | – | – |
| Glucose | – | – | 54,21 |
| Fructose | – | 52,30 | – |
| Lactulose | 11,10 | 11,44 | 11,18 |
| Yield | 100,00 | 100,00 | 100,00 |

## 6. Discussion of results of studies of structural and mechanical properties of pectin gels on apple puree with mono- and disaccharides

The study of structural and mechanical properties of pectin gels on apple puree with saccharose, fructose, glucose in the ranges of destruction and restoration, represented in Fig. 2, *a–c* and in Table 1, made it possible to establish that the pectin gels with monosaccharides differ by the larger effective viscosity in comparison to the gels on disaccharides. These patterns may be explained by the fact that at equal amounts of dry substances, the number of molecules of monosaccharides exceeds the number of molecules of disaccharides, introduced into a formulation mixture. Because of this, hydrogen bonds are formed between monosaccharides and molecules of pectin in a larger amount, which contributes to stabilization of the binding zones of pectin molecules. Hence, pectin gels on glucose and fructose possess a stronger structure.

Of scientific interest are the studies of thixotropic properties of gel systems. It was found that the formed gels on apple puree and sugars have rather weak bonds, which are destroyed under the action of mechanical action. At high shearing rate (1076 $s^{-1}$), complete destruction of the structure occurs, and its restoration is possible only by 18...22 %. This must be considered under conditions of manufacturing confectionery products, when in the course of cooling the boiled pectin-sugar masses, premature gel formation may happen before the molding. In such cases, it is not recommended to use high speeds of mechanical stirring and heating gels for its recovery to the state of sol. Analysis of thixotropic properties of the examined gel systems shows that at light mechanical load – 3...5 $s^{-1}$, the structure of masses, destroyed to the state of sol, will allow conducting the process of molding and the coefficient of thixotropy of the restored structure will amount to 85...90 %, which corresponds to the mark “excellent”. This will make it possible to obtain gel structures of confectioneryproducts of high-quality.

We found compaction of the structure of gels during storage, which is confirmed by the data of Table 2. In this case, in the sample on glucose there occurs crystallization of sugar, which intensifies over time. This is connected to the low solubility of glucose at temperatures of storage 293 K (Table 3) and by the formation of its oversaturated solution in the intermicellar dispersion medium. Thus, pectin gel with glucose is capable to acquire coagulation-crystalline structure. In order to prevent formation of crystals, it is proposed to increase the ratio of apple puree and glucose and thus draw structural and mechanical properties of the system closer to the pectin gel on saccharose. According to rheological studies (Fig. 2, *d*), it is recommended to decrease the concentration of glucose by 30 %. In this case, the values of viscosity of the undestroyed structure of pectin gel, represented in Table 1, are close to the values of the gel on saccharose. And effective viscosity of completely destroyed and restored structures is within the limits of values of the sample with fructose.

From the standpoint of creating functional confectionery products, of scientific and practical interest is the use of the disaccharide lactulose. The recommended daily amount of consumption of prebiotic is in the interval of 2...10 g per 100 g of food product, which is considerably less than the amount of sugar, necessary for the formation of pectin gel. That is why it is expedient to replace a part of sugar, introduced into the formulation of pectin gels, with lactulose. The studies, represented in Table 5, established ambiguous influence of lactulose on the structure of pectin gels. Thus, the introduction of lactulose into the composition of gels on saccharose and glucose reduces the index of effective viscosity of undestroyed structure and makes gels less elastic. Introduction of lactulose into the composition of gels based on fructose, on the contrary, increases the index of effective viscosity of the undestroyed structure and makes the gels more elastic. This is connected to differences in the indexes of solubility of the examined sugars. In particular, at 293 K (20 °C) the solubility of lactulose is larger than the solubility of saccharose and glucose, and is lower than the solubility of fructose. Consequently, the addition of lactulose to saccharose and glucose will increase their solubility and increase the amount of free moisture in the system, while the use of lactulose with fructose will decrease its solubility and reduce the amount of free moisture.

With the help of differential thermal analysis we established the total losses of moisture by the samples at the increase in temperature and determined numerical ratio of the free and bound moisture, Fig. 3, Table 6. It was experimentally confirmed that the replacement of 10 % of saccharose or glucose with lactulose contributes to the increase in the amount of free water and naturally increases the total amount of moisture, which is removed at heating. For the gels on fructose, the addition of lactulose, on the contrary, decreases the amount of free water, in connection with which such systems release less moisture at heating. The obtained data may be used for determining the temperature conditions of molding of gel masses. For example, the decrease of effective viscosity of gel-sol on saccharose or glucose with lactulose will allow reducing the temperature of pumping and flowing of confectionery mass for molding. During molding gel masses on fructose and lactulose, the temperature must be slightly increased.

However, during formation of the formulation ratios of apple puree and mixture of sugars for the functional confectionery products, it is necessary to take into account the ability of lactulose to split. This is especially important since a residual amount of lactulose may not be capable of satisfying a daily need of human organism in prebiotic. With the aid of the methods of gas-liquid chromatography we carried out research, which made it possible to find that the pectin gel with saccharose after 7 days of storage loses 11 % of lactulose, with fructose – 14,4 %, with glucose – 11,8 %.

Thus, the performed complex of research determined basic patterns of formation of structural and mechanical properties of pectin gels on mono- and disaccharides, applied in the food industry. It also enlarged scientific knowledge about the formation of pectin gels, necessary in designing products for children, dietetic and functional food.

## 6. Conclusions

1. We found that effective viscosity of pectin gel on apple puree with glucose and fructose is 1,3 times larger than the viscosity of pectin gel with saccharose. In the process of storing the gels at temperature of 293 K, their strength grows. In this case, in the gels on glucose, the formation of crystals is observed. For obtaining gel with necessary structural and mechanical properties, it is recommended to reduce the amount of glucose by 30 %. Rational ratio of apple puree and saccharose (fructose) is 1,3:1, and apple puree and glucose – 1,7:1,0. Thixotropic properties of such gels during mechanical transition of gel to sol make it possible to restore the structure by 85...90 % and conduct the process of molding.

2. It was determined that a rational amount of lactulose is 10 g per 100 g of pectin gel, which provides for the daily consumption norm of prebiotic. The formulation amount of sugar – glucose, fructose, saccharose in the composition of pectin gel must be reduced by the calculated amount of lactulose. Introduction of lactulose increases the amount of free moisture in the pectin gels on saccharose or glucose, which decreases effective viscosity of their structure. In the pectin gels on fructose, on the contrary, the addition of lactulose reduces the total amount of free moisture, which increases effective viscosity of the structure.

3. It was found that during the storage of pectin gels of functional designation, the amount of prebiotic is reduced. This necessitates the increase in lactulose in the formulations of confectionery products and recalculation of the ratio of sugar and apple puree. We calculated the compositions of apple puree and sugars taking into account the need of human organism in lactulose.

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