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STUDY OF THE FOAMING PROPERTIES OF GELATIN WITH SOLUBILIZED SUBSTANCES FOR THE PRODUCTION OF MARSHMALLOWS

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Abstract. The article presents the results of studying the foaming properties of gelatin with solubilized substances by Rauch's method. To improve the nutritional value of gelatin, deodorized refined sunflower oil with *β*-carotene was used. It has been proved that gelatin with solubilized substances can be used in the marshmallow technology with natural colourants obtained from the roselle (Hibiscus sabdariffa) and the black chokeberry. It has been established that a gelatin solution with solubilized substances has the greatest foaming ability and maximum foam stability at the rotation frequency 30–80 s^{-1} and a temperature below 45°C, with pH=3–7 within (6–8)×60 s. It has been found that aqueous extracts of natural colourants of anthocyanin origin – cryopowders obtained from the roselle and the black chokeberry – reduce the maximum foaming time to 3×60 s, as compared to water. The maximum foam stability was observed after (3–4)×60 s and was 70 and 60%, respectively, which exceeded this value of the control sample by 20–30%. The foam stability remained unchanged for (2–5)×60 s due to the presence of phenolic compounds in the extracts. 40% aqueous-alcoholic extracts of cryopowders of the roselle and the black chokeberry should be introduced after whipping the gelatin solution, since in this case, foam breaking is minimum. The foam stability increases from 60–75 to 94–99% after the introduction of 20–60% of sugar. It has been established that the use of gelatin with solubilized substances in the marshmallow technology with natural colourants from the roselle and black chokeberry makes it possible to obtain products with a density of 510–670 kg/m^3 and ensure the compliance of this quality parameter with the requirements of the current regulatory documentation.

Key words: marshmallow, gelatin, sunflower oil, β-carotene, foaming ability, foam stability, density.

ДОСЛІДЖЕННЯ ПІНОУТВОРЮВАЛЬНИХ ВЛАСТИВОСТЕЙ ЖЕЛАТИНУ З СОЛЮБІЛІЗОВАНИМИ РЕЧОВИНАМИ ДЛЯ ВИРОБНИЦТВА МАРШМЕЛОУ

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Анотація. У статті наведено результати досліджень піноутворювальних властивостей желатину з солюбілізованими речовинами методом Рауха. Для підвищення харчової цінності желатину використовували рафіновану дезодоровану соняшникову олію з β-каротином. Обґрунтовано можливість використання желатину з солюбілізованими речовинами в технології маршмелоу з натуральними барвниками з суданської троянди та чорноплідної горобини. Встановлено, що найбільша піноутворювальна здатність і максимальна стійкість піни для розчину желатину з солюбілізованими речовинами характерна за частоти обертання 30–80 $с^{-1}$, за температури менше 45°С, pH=3–7 протягом (6–8)×60 с. Установлено, що введення водних екстрактів натуральних барвників антоціанової природи – кріас-порошків із суданської троянди та чорноплідної горобини – скорочує час максимального піноутворення до 3×60 с порівняно з водою. Максимальна стійкість піни спостерігається через (3–4)×60 с і становить 70 і 60% відповідно, що перевищує значення стійкості піни контрольного зразка на 20–30%. Стійкість піни залишалась незмінною протягом (2–5)×60 с, що пов'язано з наявністю в екстрактах фенольних сполук. Введення 40% водно-спиртових екстрактів кріопорошків із суданської троянди та чорноплідної горобини доцільно після збивання розчину желатину, оскільки в цьому випадку гасіння піни буде мінімальним. Показано, що введення 20–60% цукру дозволяє підвищити стійкість піни від 60–75 до 94–99%, що обумовлено збільшенням в'язкості дисперсійного середовища. Встановлено, що використання желатину з солюбілізованими речовинами в технології маршмелоу з натуральними барвниками з суданської троянди та чорноплідної горобини дозволяє одержати вироби з густиною 510–670 кг/м^3 і забезпечує відповідність цього показника якості вимогам чинної нормативної документації.

Ключові слова: маршмелоу, желатин, соняшникова олія, β-каротин, піноутворювальна здатність, стійкість піни, густина.

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Introduction. Formulation of the problem

Confectionery is in great demand with people, especially children. Among confectionery products, not the last ones are those with a foamy structure, marshmallows. Due to their peculiar viscous consistency, pleasant taste and aroma, marshmallows lead in the confectionery market of Ukraine. Unfortunately, and not only in Ukraine, the range of marshmallow products is of low nutritional value. That is why an object of research worldwide is how to increase the nutritional value of marshmallows [1-6]. A promising way of making products (including marshmallows) more nutritious is using the phenomenon of solubilization, which allows introducing various fat-soluble additives, vitamins, natural colourants based on fat-soluble pigments, and other substances. Since solubilizing components can affect the consistency of marshmallows, it is important to study their effect on the foaming ability of gelatin.

Analysis of recent research and publications

During the last decade, solubilization in food systhems and ways of introduction of solubilized substances into food products [7-9] have been actively studied. That allowed expanding the range of highly effective food solubilizers [7], and obtaining data on the effect of various factors on the solubilization capacity of plant saponins. It has become possible to use no artificial flavours due to the development of the technology of flavoured soft drinks using essential oils of oranges, grapefruits, cinnamon, and almonds, solubilized with saponin micelles of the common soapwort (*Saponaria officinalis L.)* [8]. For further application in food technologies, solubilization of hydrophilic, lipophilic, and amphiphilic guest molecules and corresponding structural transformations are investigated [9].

The research on solubilization of sunflower oil with water solutions of Tween 80 [10] carried out in Kharkiv State University of Food Technologies and Trade is of theoretical and practical value for solving the problems of effective selection and use of nutritional supplements, vitamin components. The authors of the paper [11] continued to study organized media with sunflower oil, obtained new types of structure-forming agents (gelatin with solubilized sunflower oil, gelatin with solubilized sunflower oil and β-carotene), and determined their quality characteristics.

Marshmallows belong to the most complex types of products because of the high requirements for their structure and taste. That is why it is so important to study the foaming properties of new types of structure-forming agents to be further used in marchmallow technology.

Analysis of the literature data has shown that the foaming properties of proteins are well described. Thus, it has been proved that the wheat protein Gemtek 2100 can be used to replace part of egg protein as a foaming agent in the production of marshmallows [12]. The prospect of using dry wheat gluten as a foaming agent in marshmallow technology is shown, which allows reducing the dose of egg albumin by 30% and improving the quality of end products by decreasing the product density [13]. It has been shown [14] that due to a high content of proteins and saponins, peas and beans can be used as foaming agents in the technology of whipped cheesecake desserts.

A number of publications are dedicated to studying the foaming properties of gelatin and their dependence on its origin and structure [15], on its ingredients and technological factors [15-17]. In particular, the authors [15] have investigated the functional and technological properties of gelatin extracted from the skin of channel catfish (Ictalurus punctatus) and used in ice cream and beer technologies. It has been shown that this gelatin has a higher molecular weight and viscosity than bone gelatin and increases emulsifying capacity, emulsion stability, and foam stability (FS). The paper [16] describes the effect of black and green tea extracts on the foaming properties of gelatin. It has been shown that using 0.5–1% tea extracts leads to a 3.2–8.3% increase in the foaming ability (FA) of gelatin compared to the control sample. The effect of the new generation sugar substitutes (isomaltitol, erythritol, maltitol) and their mixtures with fructose on the foaming ability of gelatin solution has been determined. It has been established that polyols reduce the FA of a gelatin solution by 4.4–21.9% compared to sucrose. The use of sugar substitutes mixed with fructose results in a better FA of a gelatin solution proportionally to the increase in the fructose content [16]. The studies show that dietary supplements from ginseng, liquorice, and galangal roots, due to their high content of saponins, increase the FA of gelatin by 1.3–1.7 times [17].

However, the foaming properties of gelatin with solubilized substances have never been studied before. Besides, it is necessary and important for justifying the application of marshmallow technology using gelatin.

The purpose of the paper is studying the foaming properties of gelatin with solubilized substances for marshmallow manufacture. To achieve this goal, the following **tasks** have to be solved:

– to determine the rational conditions for the foam formation of gelatine with solubilized substances;

– to investigate the dependence of the foaming properties of gelatin with solubilized substances on the ingredients of the marshmallow recipe (sugar, natural colourants);

– to determine the density of marshmallows based on gelatin with solubilized substances.

Research materials and methods

Gelatin with solubilized substances is a structure-forming agent. Its components are sunflower oil and β-carotene [11]. The technology of obtaining gelatin involves solubilization of β-carotene-containing refined deodorized sunflower oil (provided by the Scientific and Production Enterprise Vitan, Ltd., Zaporizhia) with a 2%

gelatin solution, with the subsequent drying by the spraying method.

The natural cryopowders from the roselle and the black chokeberry (SPE Krias Plus, Kharkiv) were used as colourants. The technology of cryopowder production involves cryogrinding of plant material with a moisture content not exceeding 8% at a temperature of (35–70)°C into particles with a size of 10–30 microns.

Marshmallows are a foamy confectionery product. In their manufacture, gelatin with solubilized substances served as a structure-forming and foaming agent. As colourants, an aqueous or aqueous-alcoholic extract of roselle cryopowder and an aqueous-alcoholic extract of black chokeberry cryopowder were used. Marshmallows made according to Technical Specifications of Ukraine 15.8-30701488-001-2004 "Sugar confectionery. Marshmallows" were used as the control sample.

The foaming properties of gelatin solutions were studied by comparing the volume of the foam with that of the solution before whipping [18]. The ratio of the gelatin to the liquid phase was 1:10. Water, aqueous or aqueous-alcoholic extracts of roselle cryopowder, and an aqueous-alcoholic extract of black chokeberry cryopowder were used as the liquid phase. A certain amount of the gelatin solution under study was placed into a measuring cylinder at a temperature of 45 °C and whipped in a VSH 045 homogenizer till the formation of a foamy system. The foaming ability (FA, %) of gelatin was calculated by the formula:

$$FA = \frac{V_2}{V_1} \cdot 100, \qquad (1)$$

where V_1 is the volume of the gelatin solution before whipping, cm^3;

V_2 is the volume of the mixture after whipping, cm^3.

The foam stability (FS, %) was determined by the formula:

$$FS = \frac{V^{15}}{V} \cdot 100, \qquad (2)$$

where V is the initial volume of the foam, cm^3;

V^{15} is the volume of the foam after 15×60 s of whipping, cm^3.

The density of the marshmallow was determined with an apparatus including, as the main element, a glass cylinder, 400 mm high and 75 mm in diameter. A 25 cm^3 burette was welded on to its top. A plunger and a screw for fixing it at a desired height go through the centre of the cylinder in the middle of the plastic cover. The method is based on measuring the volume of toluene displaced when a weighed quantity of mashmallows is dipped into it. The density of the products (kg/m^3) was calculated by the formula:

$$\rho = \frac{m}{V_2 - V_1} \cdot 1000, \qquad (3)$$

where V_1 is the volume of a liquid that the plunger displaces in the control experiment, cm^3;

V_2 is the volume of a liquid that the plunger displaces together with the dipped product, cm^3;

m – the mass of the weighed quantity of mashmallows, g.

The absorbance of the extracts of roselle and black chokeberry cryopowders was determined with a spectrophotometer SF-2000 at the wavelength 510 nm using 10^{-2} m thick cuvettes.

Results of the research and their discussion

The foaming properties of a gelatin solution with solubilized substances have been studied in order to predict its behaviour as a structure-forming and foaming agent in the marshmallow food system.

In the process of marshmallow production, the technological factors (rotation frequency, whipping time, temperature, pH of the medium) and the recipe components (sugar, colourants, etc.) significantly influence the foaming properties of gelatin. The effect of whipping duration on the foaming ability and foam stability of the solutions under study is given in Fig. 1 (rotation frequency – 100 s^{-1}, whipping temperature – 20±1°C, initial temperature of the solutions – 45°C).

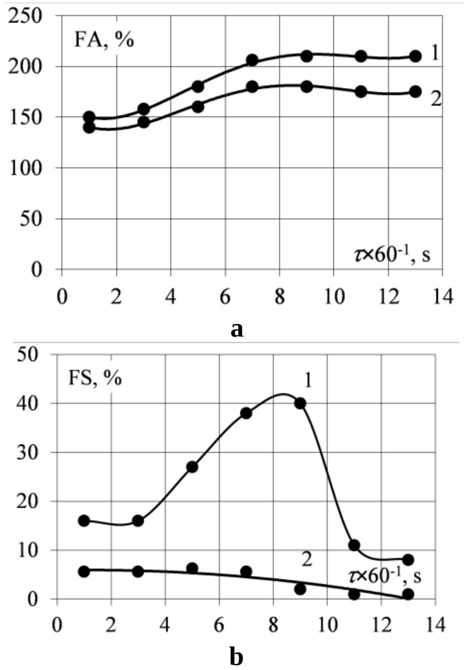
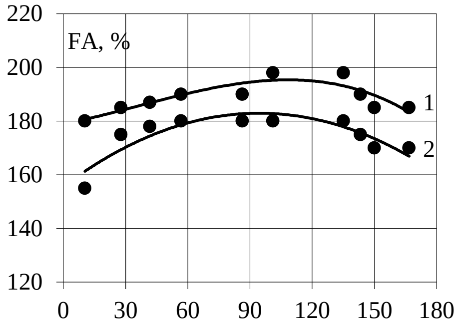


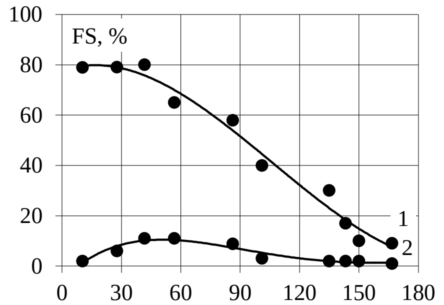
Fig. 1. The dependence of foaming ability (*a*) and foam stability (*b*) on the duration of homogenization for the gelatin solutions (1) and the gelatin solutions with solubilized substances (2)

It has been established that a thick and stable foam is formed within (6–9)×60 s for the gelatin solution, and within (6–8)×60 s for the gelatin solution with solubilized substances. Then, it collapses. The solutions of gelatin and gelatin with solubilized substances showed the same foaming tendency during the whole period of homogenization. However, the maximum foaming ability of the gelatin solution with solubilized substances is 1.2 times less than that of the gelatin solution. At the same time, the foam stability decreases by 8 times. The foam breaking can be explained by the fact that solubilized substances reduce the affinity of gelatin to the air phase. This is probably due to the hydrophobic interaction between hydrocarbon radicals of amino acids and fatty acids of triacylglycerols in the oil. Thus, the rational values for the duration of homogenization of a gelatin solution with solubilized substances are within the range (6–8)×60 s.

Fig. 2 shows how the foaming ability (a) and the foam stability (b) of gelatin solutions depend on the rotation frequency (whipping time – 8×60 s, whipping temperature – 20±1°C, initial temperature of the solutions – 45°C).



a



b

Fig. 2. The dependence of the foaming ability (*a*) and the foam stability (*b*) on the rotation frequency for the solutions of gelatin (1) and gelatin with solubilized substances (2)

Analysis of the data obtained shows that the greatest foaming ability of the solutions of gelatin and gelatin with solubilized substances is observed at the rotation frequency 30–140 s^{-1}. The further increase in the rotation frequency led to foam breaking. The maximum foam stability is determined at the rotation frequency 10–40 s^{-1} for gelatin and at 25–80 s^{-1} for gelatin with solubilized substances. The foam stability of the gelatin solution is significantly reduced at rotation frequencies greater than 80 s^{-1}, which is probably due to the formation of a lot of low molecular weight compounds after 15×60 s of whipping. They exhibit no surface activity and reduce the foam stability. Solubilized substances do not significantly affect the foaming ability of a gelatin solution, but significantly reduce the foam stability. Since the foam stability is noticeably reduced by 1.3–1.5 times at a frequency of more than 80 s^{-1} and with a sufficient foaming ability, the rational values of the rotation frequency for the gelatin solution with solubilized substances range 30–80 s^{-1}.

The results of studying the influence of the initial whipping temperature on the foaming ability of the solutions of gelatin and gelatin with solubilized substances are presented in Fig. 3 (rotation frequency – 80 s^{-1}, whipping duration – 8×60 s).

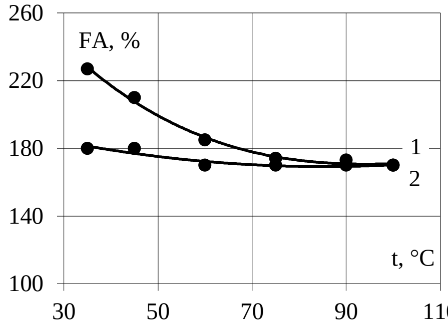


Fig. 3. The dependence of the foaming ability on the initial whipping temperature for the solutions of gelatin (1) and gelatin with solubilized substances (2)

It has been established that when the temperature increases to 55°C, the foaming ability of the gelatin solution with solubilized substances remains constant, but lower than that of the control. A further increase in the temperature reduces the foaming ability of both solutions. At 75–100°C, the foaming ability of the solutions is 170–175%. It has also been determined that when the temperature rises above 45°C, the foam stability of the solutions of gelatin and gelatin with solubilized substances significantly decreases to 3–5%. The reduction in the foaming properties is probably connected with the formation of a lot of low molecular weight compounds that exhibit no surface activity. Thus, the rational values of the temperature for the solution of gelatin with solubilized substances are within a range of 35–45°C.

Fig. 4 illustrates how the pH of the medium effects on the foaming properties of the solutions of gelatin and gelatin with solubilized substances. The pH of the solutions was changed by adding sodium hydroxide and hydrochloric acid solutions (rotation frequency – 80 s^{-1}, whipping duration 8×60 s, initial temperature of the solutions – 45°C).

Gelatin with solubilized substances forms thick foam at the pH values 4–6, which are close to the isoelectric point of gelatin (pH = 4.7–5.1). In an acidic medium, the foaming ability slightly decreases while the foam stability is 5 times higher, which is probably explained by the increased viscosity of the gelatin solution. Thus, the results obtained allow determining the rational conditions for the foam formation in the gelatin solution with solubilized substances (Table 1).

The foaming ability of the solutions of gelatin and gelatin with solubilized substances under the given conditions is 200% and 180%, respectively.It is known that not only the technological factors, but also the recipe components (sugar, colourants, etc.) significantly effect on the foaming properties of gelatin. The influence of the sugar content in a gelatin solution on its foaming properties has been studied (Fig. 5) (rotation frequency – 80 s^{-1}, wipping duration 8×60 s, initial temperature of the solutions – 45°C).

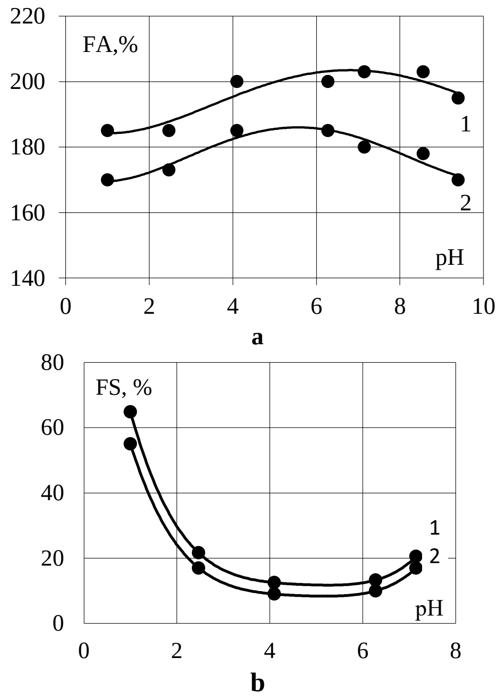


Fig. 4. The dependence of the foaming ability (*a*) and foam stability (*b*) on the pH of the medium for the solutions of gelatin (1) and gelatin with solubilized substances (2)

Table 1 – Rational conditions for foam formation in a gelatin solution with solubilized substances

Technological factor	Value of the factor for the solution	
	of gelatin	of gelatin with solubilized substances
Rotation frequency, s^{-1}	30–40	30–80
Whipping duration×60^{-1}, s	7–9	6–8
Solution temperature, °C, not more than	45	45
pH of the solution	3–7	3–7

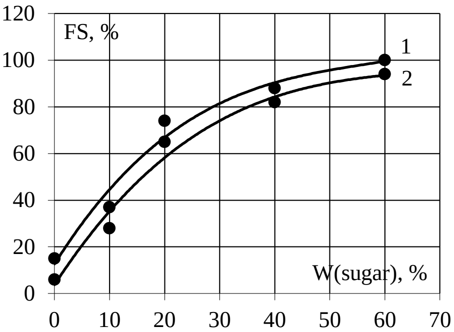


Fig. 5. The dependence of the foam stability on the sugar content for the solutions of gelatin (1) and gelatin with solubilized substances (2)

It has been determined that the foam stability increases by 60% after adding 20% of sugar. The introduction of 20–60% of sugar increases the foam stability from 60–75% to 94–99%, which is caused by an increase in the viscosity of the dispersion medium.

Natural colourants of anthocyanin origin in the form of powders and extracts are used to make the whipped confectionery pink. They can be added at different manufacture stages: swelling of the structure-forming agent, boiling the syrup, whipping the mass. So, in the next step, we investigated the influence of extracts of natural colourants of anthocyanin origin on the foaming ability of gelatin with solubilized substances.

The natural colourants used for the research were roselle cryopowder and black chokeberry cryopowder. Aqueous and 40% aqueous-alcoholic extracts acidified with citric acid were obtained from them. To determine the optimal amount of citric acid in the extract, its effect on the optical density of colourant extracts has been studied (Table 2).

According to the results obtained, the optimum extraction agents are: 1.5 and 2% citric acid solutions (to prepare aqueous extracts of roselle and black chokeberry cryopowders, respectively), and a 40% ethanol solution with the addition of 1% of citric acid (to prepare aqueous-alcoholic extracts).

The effect of the extracts on the foaming ability of the structure-forming agent has been studied on model systems. The hydromodulus of the structure-forming agent to the liquid phase was 1:10. The initial temperature of the solutions was 45°C, the whipping time – 8×60 s, the rotation frequency 80 s^{-1}. The results of the research are shown in Fig. 6.

Table 2 – Effect of citric acid content in the extractant on the optical density of the extracts of cryopowders

Cryopowder extract	Optical density at a mass fraction of citric acid, %					
	0	0.5	1	1.5	2	3
Aqueous extract of roselle crypowder	0.534	0.660	0.780	0.838	0.840	0.840
Aqueous-alcoholic extract of roselle crypowder	0.750	0.853	0.970	0.970	0.970	0.970
Aqueous extract of black chokeberry crypowder	0.130	0.136	0.150	0.155	0.160	0.160
Aqueous-alcoholic extract of black chokeberry crypowder	0.379	0.538	0.580	0.580	0.580	0.580

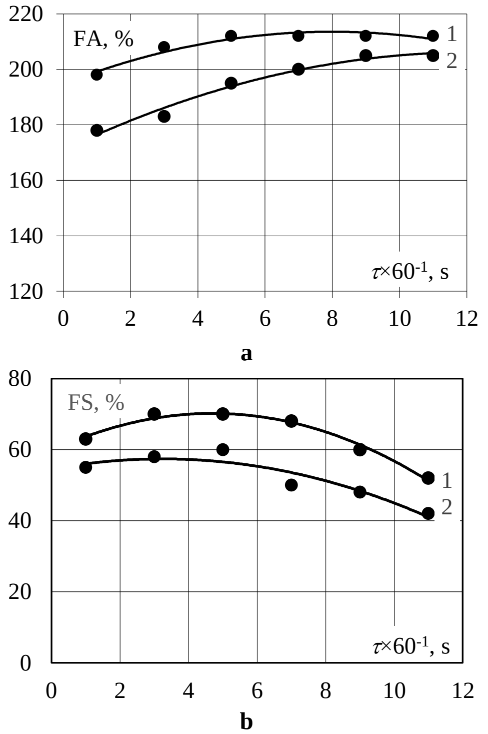


Fig. 6. Kinetic dependencies of foaming ability (a) and foam stability (b) for gelatin solutions based on an aqueous extract of cryopowder obtained from: 1 – the roselle, with addition of 1.5 % of citric acid; 2 – the black chokeberry, with addition of 2.0% of citric acid

The analysis of the data obtained shows that gelatin solutions on the basis of aqueous extracts of roselle and black chokeberry cryopowders, with addition of 1.5 and 2.0% of citric acid, respectively, have the same tendency for foaming throughout the homogenization period. Usingthe aqueous extract of roselle cryopowder as the liquid phase, instead of water, reduced the time of the maximum foam formation to 3x60 s (Fig. 1). This is explained by the presence of pectin substances in the extract. It can be assumed that hydroxyl groups in phenolic and pectin compounds of cryopowders react with amino acids of gelatin proteins with formation of associates, which contributes to more foaming and higher foam stability.The maximum foam stability of the gelatin solutions based on aqueous extracts of roselle and black chokeberry cryopowders was observed after (3–4)×60 s and was 70 and 60%, respectively, exceeding the foam stability of the control sample by 20–30%. The foam stability remained unchanged for (2–5)x60 s because of the presence of phenolic compounds in the extracts. After (6–7)×60 s from the start of homogenization, the foam stability for all systems began decreasing.

Similar results have been obtained for the gelatin solutions with solubilized substances based on aqueous extracts of roselle and black chokeberry cryopowders.

The foaming ability of the solutions of gelatin and gelatin with solubilized substances based on 40 % aqueous-alcoholic extracts of roselle and black chokeberry cryopowders, with the addition of 1 % citric acid, was significantly lower than the same parameter of the water-based sample. So, it is impractical to prepare gelatin solutions based on these extracts. To ensure the minimum foam breaking, they should be introduced only after whipping the solution of the structure-forming agent.

Thus, it has been established that aqueous extracts of roselle and black chokeberry cryopowders have a positive effect on the foam formation of gelatin with solubilized substances. The introduction of aqueous-alcoholic extracts is possible after whipping the gelatin solution since in this case the foam breaking is minimum.

The foaming properties of gelatin with solubilized substances change insignificantly compared to the control. This indicates that the traditional foaming agent used in marshmallow recipes can be replaced by gelatin with solubilized substances.

The results obtained have been used to justify and develop the marshmallow technology using solubilized substances and natural anthocyanine colourants [19,20]. Density is an important physical and chemical parameter of marshmallow quality. Its required level of up to 700 kg/m^3 results in a soft, foam-like, viscous consistency of products. Thus, the density of the new types of marshmallows based on gelatin with solubilized substances has been determined. The results obtained are presented in Table 3.

Introduction of gelatin with solubilized substances into the formulation of marshmallows slightly affects the density index. Its value for all the recipes studied (Table 3) does not exceed 700 kg/m^3 and meets the requirements of the current regulatory documentation.

Table 3 – The density of the new types of marshmallows

Variable ingredients of the marshmallow recipe		Density, kg/m^3
Colourant	**Structure-forming agent**	
–	Gelatin	524 ± 2
Aqueous extract of roselle cryopowder	Gelatin	560 ± 2
	Gelatin with solubilized substances	580 ± 2
Aqueous-alcoholic extract of roselle cryopowder	Gelatin	510 ± 2
	Gelatin with solubilized substances	530 ± 2
Aqueous-alcoholic extract of black chokeberry cryopowder	Gelatin	640 ± 2
	Gelatin with solubilized substances	670 ± 2

Validation of the results. The developed marshmallow technologies using gelatin with solubilized substances and natural colourants were introduced at four enterprises in Ukraine and abroad: confectionery factory Sweet World, Ltd., Kharkiv; CJSC KONTI PA, Kostyantynivka; sole trader S.O. Zhyrko, Kharkiv; Hotel and Restaurant Complex Antek – Confectionery Jaglo (Zlinice, Poland). Two utility model patents have been obtained, process and manufacturing specifications for the new products have been developed and approved in accordance with the established procedure.

Conclusion

The rational conditions of foaming of gelatin with solubilized substances have been determined. It has been established that the introduction of natural colourants, aqueous extracts of roselle and black chokeberry cryopowders, reduces the time of maximum foaming to 3×60 s, compared to water. At the same time, their foam has the maximum stability after (3–4)×60 s and is 70 and 60%, respectively, which exceeds the foam stability of the control sample by 20–30%. The aqueous-alcoholic extracts should be introduced after whipping the gelatin solution. It has been shown that the introduction of 20–60% of sugar results in an increase in the foam stability from 60–75 to 94–99%. It has been established that the density of the new marshmallow types meets the requirements of the current regulatory documentation and is 510–670 kg/m^3.

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