1. Introduction

The range of flour-based confectionery covers a large group of food products – various types of cookies, waffles, gingerbread, muffins, cakes. However, studies into their chemical composition, biological and nutritional value prove that these products are poor in proteins, dietary fiber, vitamins, and minerals [1, 2]. Therefore, one of the most popular modern direction in the confectionery industry development is to organize the production of flour confectionery for functional and recreational purposes, which will contain scarce and valuable compounds and elements [3].

Calcium is a macro element that plays an important role in the normal development and functioning of the human body [4]. About 2.0 % of an adult’s body weight falls on this element. The daily need for calcium for people of all ages ranges from 1,000 to 1,500 mg/day [5]. Calcium is found in many products, but it is available in small quantities,
which is not enough to ensure the daily rate of a person. Calcium deficiency is inherent in up to 90% of the population of many countries, which leads to the development of diseases. Doctors confirm the link between calcium deficiency in the human body and the occurrence of a number of diseases such as osteoporosis, colorectal cancer, breast cancer, kidneys, prostate, ovaries, stomach, cardiovascular pathologies, etc. [6].

It is known that the best natural source of digestible calcium compounds are natural dairy products [7]. It was established that the protein-mineral form of milk calcium, namely caseinate, makes it possible not only to maintain a certain level of calcium in the blood but also to transfer and accumulate it in tissues. However, under modern conditions of urbanization of the population, the use of these products is limited due to a number of reasons, including social, and, as a result, it cannot provide the human body with the necessary amount of calcium-containing compounds.

Taking into consideration the above problem, food industry specialists, in order to enrich food products with the specified nutrient, including flour confectionery, propose to introduce new calcination techniques. Of these, the most known are the use of mineral low-molecular organic forms of calcium citrate, calcium lactate [8, 9], egg shell processing products [10–12], and food bone [13, 14], dry calcium caseinate [15]. However, these forms provide only the maintenance of calcium levels in the blood and do not guarantee its absorption and circulation in tissues.

Thus, the substantiation of the technology of buttery biscuits enriched with natural absorption of calcium compounds by introducing protein-mineral supplement [16] into product formulation is promising. The scientific literature [1] reveals that the emulsion is one of the main semi-finished products for butter biscuits, whose properties, structural and mechanical characteristics, and stability greatly affect the consumer properties of the finished product. Taking into consideration the chemical composition and technological properties of the protein-mineral additive, it is a relevant task to study its effect on the properties of the emulsion to obtain dough for butter biscuits.

### 2. Literature review and problem statement

At present, several ways to improve the quality of the emulsion during the production of butter biscuits are known. Paper [17] reports the results of studying the qualitative indicators of the butter biscuit emulsion using a combined fat base (replacement of 30% margarine with sunflower oil) and meal of cedar and walnuts. It was established that when using only the combined fat base, the resistance of the emulsion decreases, and the introduction of additional meal of nut raw materials (up to 40%) makes it possible to increase this indicator and bring it closer to control. However, to determine the emulsion stability indicator, the developers apply the method of emulsion centrifugation without heat treatment. The consequence of using this method is the lack of study of the specified indicator during the heat treatment of the emulsion, and, accordingly, insufficient study of the preservation of emulsion characteristics in the product baking process.

A similar approach is employed in works [18–20], whose authors studied emulsion resistance indicators during its minor heat treatment (at 40°C). Using the specified parameters cannot make it possible to accurately determine the above indicator in the process of baking cookies. Paper [18] considers the effect of mushroom powder, flax meal, a composition of beet powder and rapeseed powder, a composition of beet powder, rapeseed powder, and milk thistle meal on the quality indicators of the emulsion system. It was established that adding them to the formulation of long cookies leads to an increase in the emulsion density by 20%, 24%, 22%, and 27%, respectively. Increasing the density and, as a result, the viscosity of the emulsion, significantly increases its stability. The reported results confirmed the need to introduce flax meal and milk thistle meal directly into the dough together with flour during mixing. Paper [19] states that using pumpkin puree and pumpkin seed meal in the long cookies formulation would also lead to similar results (an increase in the viscosity and density of the emulsion). This effect is explained by the presence in the introduced raw material of a significant amount of dietary fiber, which actively absorbs and binds free water, which positively affects the stability indicator and improves the quality of the emulsion. The results of determining the effect of cross-linked starch and milk isolate on the quality indicators of the emulsion system of long cookies are given. The stability of the emulsion increases, respectively, by 2.5 and 2.7 times, compared to the control sample. According to the authors, this is due to the active binding of moisture with the specified raw material whose water-absorbing capacity is much higher than the water-absorbing capacity of flour. This property has a positive effect on the emulsion stability indicator and increases its quality; however, it can cause difficulties in transportation. That predetermined the expediency to add only isolated milk protein to the emulsion, and to add the cross-linked starch together with flour [20].

The results reported in [18–20] allow their authors to assert that the use of those methods has made it possible to solve partially the technological aspects of biscuit production; however, the issue of enrichment of products with mineral compounds is not taken into consideration.

In works [21, 22], the possibility of using bleached wax oil from rice bran and emulsion gel based on inulin (inulin and olive oil) is proposed. Based on the results from experiments, it is noted that the prepared emulsion containing these components has high stability, and finished products have a reduced fat content. However, the use of these components in the formulations of flour confectionery can complicate the technological process of their production. The reason for this may be the following difficulties — the difficulty in obtaining olio gels and the high content of wax in them, which can lead to their curd. In order to prevent this phenomenon, it is advisable to temper the olio gels in the temperature range of 25–30°C. This, in turn, would lead to additional material costs, as well as require additional control over the operation of dosing equipment.

It is noted in [23] that it is possible to use in the formulations of bakery and flour confectionery products (in general) of partially skimmed flour from sapucaya walnut (Lecythis pisonis Cambess). This is confirmed by the indicators of its functional characteristics, such as emulsification (8–20 m²), foaming (6–12%), and ab-
sorption capacity of water (0.35–1.38 g/g of flour) and oil (0.72 – 1.57 g/g of flour). Such flour is effective in obtaining emulsions with a fine structure (drops of micrometer size up to 15.0 microns) with its predicted stability. However, the mass implementation of the use of these raw materials is complicated. The reason for this may be the high cost of raw materials and the limited cultivation area of this crop. An option to overcome the related difficulties may be the use of alternative raw materials with a wider distribution area and similar technological properties, for example, sesame and chia grains, sunflower seeds.

Our review of the above data suggests that it is advisable to conduct a study into the interaction between a protein-mineral supplement and the components of the emulsion system in the composition of butter cookies. The results to be obtained would make it possible to adjust their formulation ratio, as well as the parameters of the technological process, in order to make products enriched with calcium, of high quality.

3. The aim and objectives of the study

The aim of this work is to determine the effect of protein-mineral additives on the properties of the butter biscuit emulsion. This could make it possible to form the health and dietary properties of the finished product and positively affect the formation of its structural and mechanical characteristics.

To accomplish the aim, the following tasks have been set:
– to determine the conditions of hydration of the protein-mineral additive and the protein-mineral improved additive in cow’s milk before emulsification;
– to determine the emulsifying capacity and stability of emulsions of systems using protein-mineral additives;
– to investigate the effect of protein-mineral additives on the viscosity characteristics of emulsions.

4. The study materials and methods

4.1. The study materials

Our experimental study was carried out at the laboratories “Rheological research”, “Actual problems of technologies of bakery, confectionery, pasta and food concentrates”, “Medical and biological problems of food technology”. The laboratories are part of the Educational and Scientific Institute of Food Technologies and Business, Kharkiv State University of Nutrition and Trade (Ukraine).

The study used a protein-mineral additive (PMA) and an improved protein-mineral additive (IPMA) [24], which are manufactured under laboratory conditions in accordance with TU U 10.8-01566330-281:2013 “Enriching protein-mineral additives”. The additives are a powdery cream-colored system with a neutral aroma and taste. In terms of chemical composition, additives are partially thermally hydrolyzed collagen proteins, which are a matrix for the formation of chelate complexes with calcium and magnesium. In additives, calcium compounds are found in two states: chelate complexes and calcium citrates. That makes it possible, on the one hand, to provide calcium deposition in tissues through the high metabolic activity of chelate complexes, as well as maintain calcium levels in the consumer’s blood due to citrates. The improved form of the additive contains up to 20 % of chondroitin sulfates, which belong to heteropolysaccharides, have pronounced complex-forming properties, and are an important metabolic factor that ensures the effective absorption of calcium compounds and its accumulation in tissues. The chemical composition of the additives is given in Table 1 [24].

### Table 1

<table>
<thead>
<tr>
<th>Indicator name</th>
<th>Chemical composition of protein-mineral additives</th>
<th>Protein-mineral additive</th>
<th>Improved protein-mineral additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture mass share, %</td>
<td>6.1±0.2</td>
<td>6.2±0.2</td>
<td></td>
</tr>
<tr>
<td>Protein mass share, %</td>
<td>75.5±2.75</td>
<td>60.2±2.5</td>
<td></td>
</tr>
<tr>
<td>Fat mass share, %</td>
<td>8.1±0.4</td>
<td>6.5±0.3</td>
<td></td>
</tr>
<tr>
<td>Chondroitin sulfate mass share, %</td>
<td>0.2±0.005</td>
<td>19±1.0</td>
<td></td>
</tr>
<tr>
<td>Ash mass share, %, including</td>
<td>10.1±0.4</td>
<td>8.1±0.3</td>
<td></td>
</tr>
<tr>
<td>Calcium mass share, %</td>
<td>7.5±0.4</td>
<td>6.7±0.0.35</td>
<td></td>
</tr>
<tr>
<td>Magnesium mass share, %</td>
<td>0.35±0.02</td>
<td>0.31±0.02</td>
<td></td>
</tr>
</tbody>
</table>

The special feature of both protein-mineral additives is pronounced calcium-donor properties, which are manifested due to the partial dissociation of calcium citrate. At the same time, an PMA has a higher overall protein and calcium content compared to an IPMA. This predetermines the effectiveness of using the PMA as an emulsifier and enriching additive. However, the improved form of the additive contains chondroitin sulfates, which, like hydrocolloids and heteropolysaccharides, can increase the viscosity of aqueous solutions. That could significantly affect the stabilization of emulsions and prevent the coalescence of the fat phase. Physiologically, the supplements have no age restrictions and can be used in mass consumption food technologies. Physiologically, the amount of their use is limited by the general requirements for the content of the target nutrient in fortified products (not exceeding 30 % of the daily need for a conditional portion of the product).

Our study also used cow’s milk with a fat content of 2.5 %, mélange from chicken eggs, refined and deodorized sunflower oil, butter with a 72.5 % fat content. Model emulsions were prepared under laboratory conditions at an emulsification rate of 200 s⁻¹ over 5×60 s.

4.2. Methods for determining the effect of protein-mineral additives on the emulsifying capacity, stability, and viscosity of butter biscuit emulsion

The effective viscosity of the systems was determined at the rotary viscometer with a stable shear voltage VNP – 0.2 M. The additives were swollen in the environment of cow’s milk at a temperature of 20±2 °C.

We studied the emulsifying capacity by determining the inversion point of phases [25]. The experiment used a four-component system (50 g) based on mélange, the hydrated additive in the environment of cow’s milk (milkaddi-
The share of the destroyed emulsion (%) was determined as the sum of the fat and aqueous phases (%), separated after centrifuging ($t=5\times60\text{ s}$, $\gamma=1,500\text{ min}^{-1}$) before and after heat treatment ($t=90...95\text{ °C}$, $t=3\times60\text{ s}$). The stability of the emulsion was defined as a share of the non-destroyed emulsion (%) [25].

The microscopy of emulsions was carried out at the microscopes Granum W1001 by coloring emulsions with methylene blue. We used an achromatic lens ($\times10$) and a wide-field eyepiece Wf10x/18.

Statistical treatment of the results employed the software tool Microsoft Excel 2016. The experimental studies were carried out with five-time repeatability ($n=5$). The error in all experiments did not exceed 5 %, the probability of approximation:

\begin{align*}
R^2 &= 0.9915, \\
R^2 &= 0.9927, \\
R^2 &= 0.9966.
\end{align*}

5.2. Determining the emulsifying capacity and stability of emulsions of systems using protein-mineral additives

An important characteristic of emulsion systems is the emulsifying capacity, which is characterized by the system's ability to hold a "direct" emulsion while maintaining the fat fraction as a fat phase. The results of studying the emulsifying capacity of the systems are shown in Fig. 2.

The resulting dependences are described by the following approximation equations with the corresponding accuracy of approximation:

1. $y=-0.4264x^2+7.3307x+41.071$, $R^2=0.9915$.
2. $y=-0.4935x^2+8.8017x+44.286$, $R^2=0.9879$.

One can see that the maximum emulsifying capacity was observed when using PMA in the system with the ratio of hydrated additive:melange of 3.7...2.8. When applying IPMA, the maximum capacity was observed in the system hydrated additive:melange 1:9.

At the next stage, we studied the emulsion stability. This characteristic is important in terms of determining the ability of the emulsion to destroy and coalescence with the fat phase, which is negative in terms of the formation of the properties of butter biscuits. We determined the amount of the released water and fat phases. The emulsion samples were colored and investigated under a microscope. The results are shown in Fig. 3–6.

The charts in Fig. 3, 4 demonstrate that the amount of the released fat and water fractions decreases with an increase in the content of both PMA and IPMA, which indicates an increase in the emulsion stability. One can see that the emulsion stability is higher in samples containing 5–7 % of IPMA. This is confirmed by the micrographs in Fig. 5, 6 that indicate the emulsion structure is retained after heat treatment. In the samples that contained IPMA there is a smaller aggregation of the fat phase and the destruction of the emulsion system.
5.3. Studying the effect of the protein-mineral additive on the viscosity characteristics of emulsions

At the next stage, we investigated the viscosity of emulsions obtained using IPMA. The viscosity of the emulsion is an important indicator of the sedimentation stability of the dispersed system. It depends on a series of factors. The first is the viscosity of the water environment (in the case of analysis of “direct” emulsions). The high viscosity of the water environment prevents the coalescence of the fat phase. At the same time, the high dispersion and homogeneity of the fat phase distribution would also have a positive effect on the viscosity of the emulsion and, as a result, its stability. The third factor is the type of fat used to hold the emulsion. As a fat phase, butter with a fat content of 72.5% was used. The results of our study into the effective viscosity of emulsions are shown in Fig. 7.

The derived dependences are described by the following approximation equations with the corresponding accuracy of approximation:

1. $y=650,2x^{1.026}$, $R^2=0.9788$.
2. $y=715,44x^{-0.82}$, $R^2=0.9782$.
3. $y=820,66x^{-0.663}$, $R^2=0.9876$.
4. $y=893,54x^{-0.579}$, $R^2=0.9867$.
5. $y=1036x^{-0.533}$, $R^2=0.9791$.

The data shown in Fig. 7 demonstrate that with an increase in the content of the additive, there is a pronounced increase in the viscosity of the emulsion, even if the fat content decreases. This trend is most pronounced with the content of IPMA at the level of 3–5 %.
6. Discussion of results studying the effect of protein-mineral additives on the properties of the emulsion of butter cookies

Preliminary hydration of powdered additives makes it possible to fully realize the functional properties of their ingredients. Viscosity measurement makes it possible to estimate the degree of hydration of polymers. The data in Fig. 1 demonstrate that over time, the viscosity of colloidal solutions at the same shear rate ($\gamma = 50$ s$^{-1}$) and system temperature ($t=20 \pm 2^\circ$C) increases. It is characteristic that the viscosity of systems with a content of 5% of the additives is greater compared to systems containing 3% of the additives. The greatest viscosity is observed in the systems formed using 5% of the IPMA. One can see that when such a system is hydrated after 21×60 s, the viscosity does not increase, so the hydration of polymers has passed completely.

Complete hydration of the additive polymers is important in terms of the implementation of its technological properties by increasing the viscosity of the dispersed environment, stabilizing the “direct” emulsion, and keeping the dispersed system from the coalescence of the fat phase. Analysis of the maximum achieved values of effective viscosity of the systems makes it possible to conclude about the rational time of hydration. The rational modes for the pre-hydration of additives before emulsification in the environment of cow’s milk are $t=20 \pm 2^\circ$C, and the following time: 3% PMA and IPMA – (12...15)×60 s; 5% PMA – (15...18)×60 s; 5% IPMA – (21...24)×60 s.

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Our analysis of photographs in Fig. 6 reveals a much greater aggregation of the fat phase in the emulsion, which is made using PMA (Fig. 6, a). The sample with PMA (Fig. 6, a) has a more pronounced coalescence of the fat phase. That causes the worse stability of this emulsion after heat treatment. In the emulsion made using IPMA (Fig. 6, b), there is a general preservation of a finely dispersed emulsion structure. Only single aggregation of fat balls is observed. Thus, the positive effect of additives on the emulsifying capacity and stability of the emulsion has been proven. The advantage of an improved form of supplement over its standard form has been proven. The results of emulsion stability hold exclusively for the specified systems based on plant-derived refined oil. However, the general trends are fair for those emulsion systems that were obtained using other fat-containing raw materials.

Thus, the use of IPMA in the amount of 5% is more rational in terms of ensuring the stability of the emulsion.

The reported results of our study into the viscosity of the finished emulsions correlate well with the above results. The increase in the viscosity of the emulsion is due to the thickening of the dispersed environment, better finely dispersed distribution of the fat phase in samples containing 5...7% of IPMA, and probably a large surface of interphase interaction by stabilizing the finely-dispersed emulsion system. The resulting viscosity values are true for emulsion systems at a temperature of $20 \pm 2^\circ$C, based on butter. Subject to the aforementioned condition, the resulting trends would hold for emulsion systems produced using other fat-containing raw materials.

When analyzing the results, we can conclude that the use of IPMA in the amount of up to 7% is more rational and makes it possible to obtain more stable emulsion systems with a better emulsifying capacity. Thus, the application of protein and mineral supplements makes it possible to contribute to solving a complex issue related to nutrition science and enrichment of diets with deficient calcium compounds, and improvement of the technology for making butter cookies.
Our results are important from the point of view of adjusting the formulation composition of confectionery products using protein-mineral additives and ensuring high quality characteristics, in particular, structural and mechanical, of the finished product.

Further research will aim at studying the qualitative characteristics of flour confectionery products prepared by using an improved protein-mineral additive.

7. Conclusions

1. The use of protein and mineral additives based on hydrolyzed collagen structures in the amount of up to 7% makes it possible to positively affect the quality of emulsion systems of buttery flour confectionery products. The rational conditions for the pre-hydration of additives in cow’s milk environment have been established: \( t = 20 \pm 2^\circ C \), and the following time: 3% PMA and IPMA – (12...15) \times 60 \, s; 5% PMA – (15...18) \times 60 \, s; 5% IPMA – (21...24) \times 60 \, s. It is proven that the use of protein-mineral additives makes it possible to provide for a high emulsifying capacity of the systems. It has been determined that the maximum fat content as part of the “direct” emulsion of the system hydrated PMA:melange could equal 58±2% when using PMA, and 63±2% when using IPMA.

2. The use of up to 7% of the additives makes it possible to ensure better stability of the emulsions, including after heat treatment. It is established that if one uses 5...7% of IPMA, it is possible to ensure the preservation of the emulsion system after heat treatment at the level of 78...82%. The stabilization of emulsions is mainly due to an increase in their viscosity. The described effect on the quality of emulsions makes it possible to ensure consistently high structural and mechanical characteristics of flour confectionery products.

3. The application of IPMA has a number of advantages compared to PMA. It has been established that the IPMA provides for better stability of emulsion systems, including after heat treatment, their greater emulsifying capacity, which is associated with the stabilizing properties of chondroitin sulfates. The use of protein-mineral additives makes it possible not only to enrich finished products with digestible calcium compounds but also to positively affect the technological and consumer characteristics of the finished product.

References


