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INFLUENCE OF RAW MATERIALS ON THE CHANGE OF CRYSTAL STRUCTURE OF GINGERBREAD IN THE STORAGE PROCESS

В роботі проведено аналіз сучасних методів дослідження процесу черствіння борошняних кондитерських виробів, а саме рентгенофазного аналізу, дифракції рентгенівських променів, диференціальної скануючої колориметрії. Оскільки кристалічну структуру готових борошняних кондитерських виробів формують безпосередньо крохмаль, цукор та інші вуглеводи, а процеси, пов'язані з утриманням в них вологи, впливають на їх зберігання. Для проведення дослідження процесів черствіння використано метод рентгенофазного аналізу на дифрактометрі ДРОН-УМ-1 (Росія), що виявляє ступінь та типи деформації кристалічної структури речовин. Дифракційні максимуми крохмалю досліджено при значеннях кутів відбиття в межах 10–30°. Об'єктами дослідження були авторські пряники «Бджілка» та «Імбирні пікантні», а за базовий зразок до порівняння обрано пряники «Північні».

До рецептури запропонованих пряників вносили наступну сировину:

- «Бджілка» – борошно житнє обдирне, солод житній ферментований, мед штучний, олія соняшникова, молоко сухе знежирене, повидло яблучне, пілок бджолиний, порошок суцвіт'ям тим'яну повзкого;
- «Імбирні пікантні» – борошно житнє обдирне, житній солодовий екстракт, інвертний сироп, суха підсирна сироватка, порошок кореня імбиру, порошок суцвіт'ям бузини.

В результаті проведення рентгенофазного аналізу досліджено ступінь руйнування кристалічної решітки крохмалю в структурі м'якуша розроблених пряників. Проаналізовано взаємодію крохмалю з іншими вуглеводами та їх вплив на формування остаточної кристалічної структури готових виробів та зміни кристалічної структури впродовж зберігання. Вивчено процеси черствіння пряників свіжих, після 2 і 4 місяців зберігання, на які впливають процеси самоасоціації, гідротворення моно- та дицукридів, деградації та ретроградації крохмалю.

Виявлено особливості процесу черствіння після 2 і 4 місяців зберігання за допомогою аналізу піків дифрактограм. Проаналізовано процес ретроградації крохмалю у готових виробах на основі отриманих дифрактограм та доведено здатність використаних натуральних добавок у пряниках подовжувати термін їх зберігання. Результати даних досліджень можна впроваджувати у кондитерській промисловості з метою виробництва продукції з подовженим терміном зберігання.

Ключові слова: борошняні кондитерські вироби, нетрадиційна сировина, кут дифракції, інтенсивність дифракційного максимуму, рентгенофазний аналіз.

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1. Introduction

During storage of flour confectionery products, free water migrates in the crystalline areas of starch, where it becomes bound and causes staling of the products. Therefore, with the formation of stable hydrates of mono- and disaccharides, the process of water migration and staling of gingerbreads is inhibited [1]. The loss of free moisture during the retrograde of starch is compensated by the loss of moisture by the carbohydrate. Therefore, the more stable the hydrate is mono- and disaccharides, the slower the gingerbreads are stale.

Starch is soluble in water, although when heated it partially adsorbs water, its crystal structure is destroyed as

a result. In the presence of mono- and disaccharides, the migration of water of the heterogeneous phase of starch is reduced, and in the presence of fructose and glucose a certain amount of water is released, interacts with starch, glutenins and gliadin, forming gluten [2].

The structure formation of flour confectionery products is influenced by the processes of self-association, hydrotreatment of mono- and disaccharides, degradation and retrograde of starch, it is their course that has become the object of study during the storage of new gingerbread cookies. Starch, sugar and other carbohydrates are directly involved in these processes, which form the crystalline structure of the finished products and are associated with the moisture content during storage.

Table 1

Features of the recipe composition of new gingerbread

Prescription components	The amount of raw materials in the recipe for gingerbreads, kg/t		
	Pivnichni control	Bdzhilka	Imbyrni Pikantni
Wheat flour 1 grade	508.68	348.16	380.23
Peeled rye flour	–	127.09	126.75
Fermented rye malt	–	26.82	–
Rye malt extract	–	–	27.04
White crystalline sugar	337.80	274.43	288.16
Artificial honey	–	105.69	–
Starch syrup	96.72	59.29	84.50
Margarine	–	24.54	32.17
Sunflower oil	14.63	16.94	–
Skimmed milk powder	–	21.50	–
Apple jam	–	25.41	–
Ammonium carbonate	4.42	4.24	5.07
Drinking soda	1.46	1.54	1.70
Cocoa powder	–	9.72	–
Bee pollen	–	0.56	–
Creeping thyme inflorescence powder	–	1.43	–
Invert syrup	–	–	52.74
Dry cheese whey	–	–	27.4
Ginger root powder	–	–	2.54
Elderberry inflorescence powder	–	–	0.51
Essence	2.88	–	–

For conducting relevant studies, X-ray phase analysis is the most optimal; it relates to X-ray analysis methods, precisely because of its availability, speed and ease of interpretation of the results, as well as the ability to identify the degree and types of deformation of the crystal structure.

Method of X-ray diffraction in the study of changes in the crystal structure of cookies is widely known. One of the main reasons for stale flour confectionery is stained is the release of moisture from the sugar crystal lattice – sucrose recrystallization. That is why trisaccharide – raffinose is used in the formulation in order to slow down this process [3].

The method of differential scanning calorimetry is used to study the crystal structure of bakery products (this method, by analogy, can be used for gingerbread). An endothermic melting transition of crystalline amylopectin at 70 °C is revealed. The method of X-ray diffraction analysis for bread shows a relative crystallization of starch at the level of 36–41 %, and the method of differential scanning calorimetry – 32–43 %. Due to its simplicity and sufficient availability, an X-ray phase analysis is chosen [4].

The X-ray phase method and differential scanning calorimetry are used to study the relationship between the amount of damaged starch, the density of the bread crumb, the degree of retrograde of amylopectin, which characterizes the peculiarities of stale bread. Damage to starch increases the retrogradation degree of starch, the flesh hardens [5].

The objects of research are developed according to the author's recipes «Bdzhilka» and «Imbyrni Pykantni» gingerbreads [6, 7], and the gingerbread «Pivnichni» gingerbreads are used as a comparison sample [8]. The recipe for the developed gingerbread is made by peeled rye flour, rye grain processing products, beekeeping products, milk processing products, apple jam, and medicinal plant powders. Fermented rye malt and rye malt extract are used from rye grain processing products; beekeeping products – artificial honey, bee pollen, dairy products processed products – skimmed milk powder and dry whey powder. From medicinal plants, creeping thyme inflorescences powder, ginger root powder, elderberry inflorescence powder are used [9]. The contents of the individual prescription components are presented in Table 1.

The aim of research is to study the degradation degree of the starch crystal lattice in the pulp structure of the developed gingerbreads.

In the process of achieving the goal, research was conducted on the processes of interaction of starch with other carbohydrates and their influence on the formation of the final crystalline structure of finished products. The basis of the research is the study of changes in the crystal structure during storage.

2. Methods of research

To determine the phase composition of substances, an X-ray phase analysis is used to reveal the degree of deformation of the crystal structure and the types of its defects. The products are studied on a DRON-UM-1 X-ray diffractometer (Russia), tube type 1.5 BSV23 Cu (Fig. 1).

Samples of the studied gingerbreads with a thickness of 2 mm are used, diffraction patterns are recorded under the conditions of the same area of the studied material and the intensity of radiation. The values of the reflection angles range from 10–30°, this is due to the values of the diffraction maxima of starch [10].

The X-ray phase analysis method is based on the fact that for X-rays the crystal lattice is diffractive. In the interaction of crystalline material with monochromatic X-rays, there is always a certain number of crystals for each kind of planes that fall into the reflection position. In this case, at a certain angle, a diffraction maximum for a given kind of planes will be observed. If the object under study consists of several phases, then each phase will have a unique diffraction pattern. In this case, the diffraction patterns are the superposition of the diffraction patterns of all phases in the sample under study. And the intensity of the reflexes of each phase will depend on its amount in the dough mixture [11, 12].



Fig. 1. DRON-UM-1 X-ray diffractometer

3. Research results and discussion

The study of the destruction degree of the crystalline structure of starch custard gingerbread is done. The influence of the characteristics of the recipe composition of the developed gingerbread on the dynamics of moisture

loss and a change in the crystal structure of gingerbread is studied. The effectiveness of the added additives to the gingerbread recipe is shown by a change in the crystal structure during 4 months of storage. These changes in the crystal structure of custard gingerbread during storage are shown in Fig. 2.

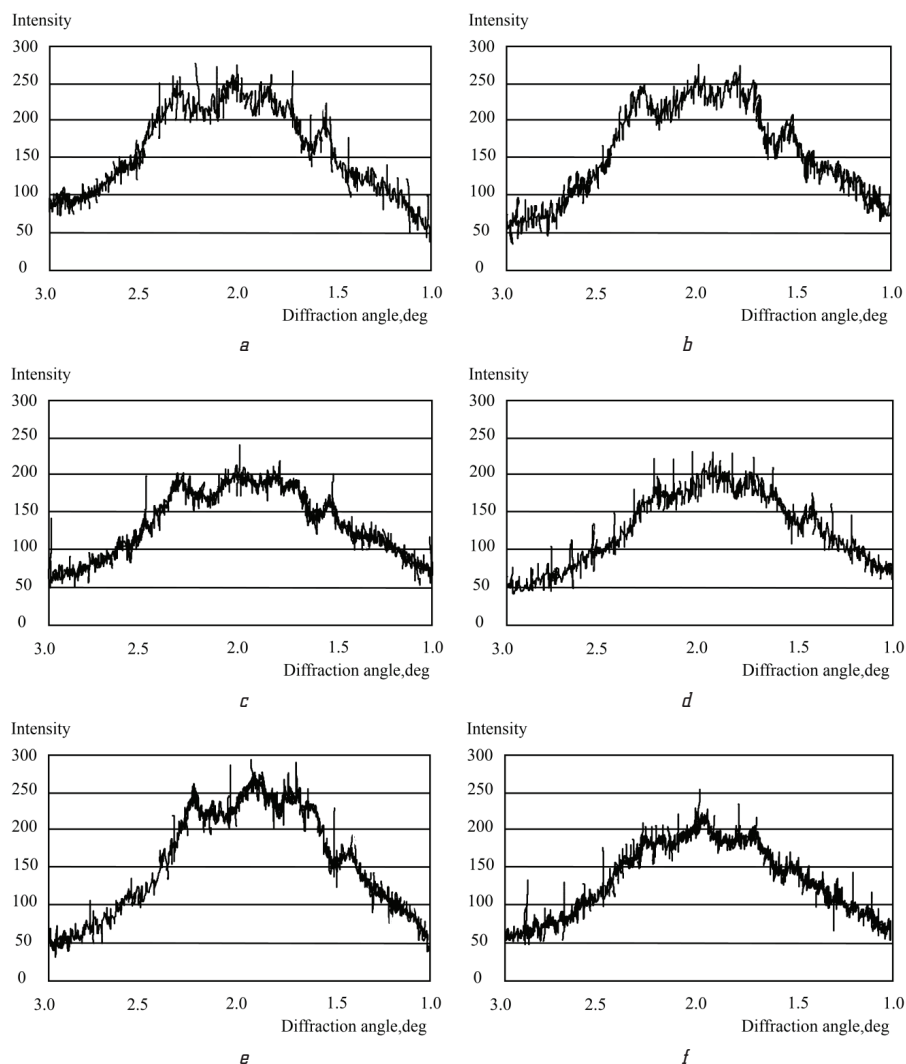


Fig. 2. The diffraction patterns of the control sample of gingerbreads and «Bdzhilka» gingerbreads:
a – control sample fresh; *b* – control sample after 2 months of storage; *c* – control sample after 4 months of storage; *d* – «Bdzhilka» gingerbreads fresh;
e – «Bdzhilka» gingerbreads after 2 months of storage; *f* – «Bdzhilka» gingerbreads after 4 months of storage

At the beginning of storage, the crystal structure of the control sample of gingerbread is most expressive. This may indicate insufficient destruction of starch molecules and their conglomeration with sucrose molecules. The presence of diffraction maxima at 13° (in noise), 15, 19, 20, and 23° indicates the presence of crystalline sucrose in the dough of the control sample of gingerbread. This is due to the consumption of water by a saturated solution of sucrose, and the occurrence of a supersaturated solution, followed by its partial crystallization. Positive is the use of a smaller proportion of sugar and the introduction of most of the fructose due to artificial honey and the use of fermented rye malt and peeled rye flour. This contributes not only to a more complete destruction of the crystalline structure of starch, but also prevents the formation of a supersaturated solution of sucrose, thereby ensuring the content of most of the moisture.

During two months of storage in «Bdzhilka» gingerbread, diffraction maxima of 19 and 20° appeared, which is explained by partial crystallization of sucrose. After storing gingerbread data for 4 months, peaks characteristic of the crystalline structure of starch are visible, but they are of

low intensity. In the control sample, sucrose recrystallization took place in the second month of storage; therefore, the intensity of the maxima increased, and at the end of storage, due to moisture loss, five peaks of low intensity characteristic of starch are observed.

The use of rye malt extract and invert syrup without acid neutralization also contributes to an increase in the proportion of fructose in «Imbyrni Pikantni» gingerbreads. Therefore, almost complete destruction of the crystalline structure of starch and sucrose is achieved, as evidenced by low intensity maxima at 13° and 19° (in noise), 15 and 23° (Fig. 3).

After two months of storage in «Imbyrni Pikantni» custard gingerbread, partial stratification of starch molecules occurred and five characteristic maxima of starch became noticeable. By the end of storage, a partial loss of moisture occurred due to the supersaturation of the sucrose solution, the release of moisture by the sucrose molecule and the restoration of its crystalline structure, so the intensity of diffraction peaks increased sharply by 15 and 23°. This could be observed in the control sample after two months of storage.

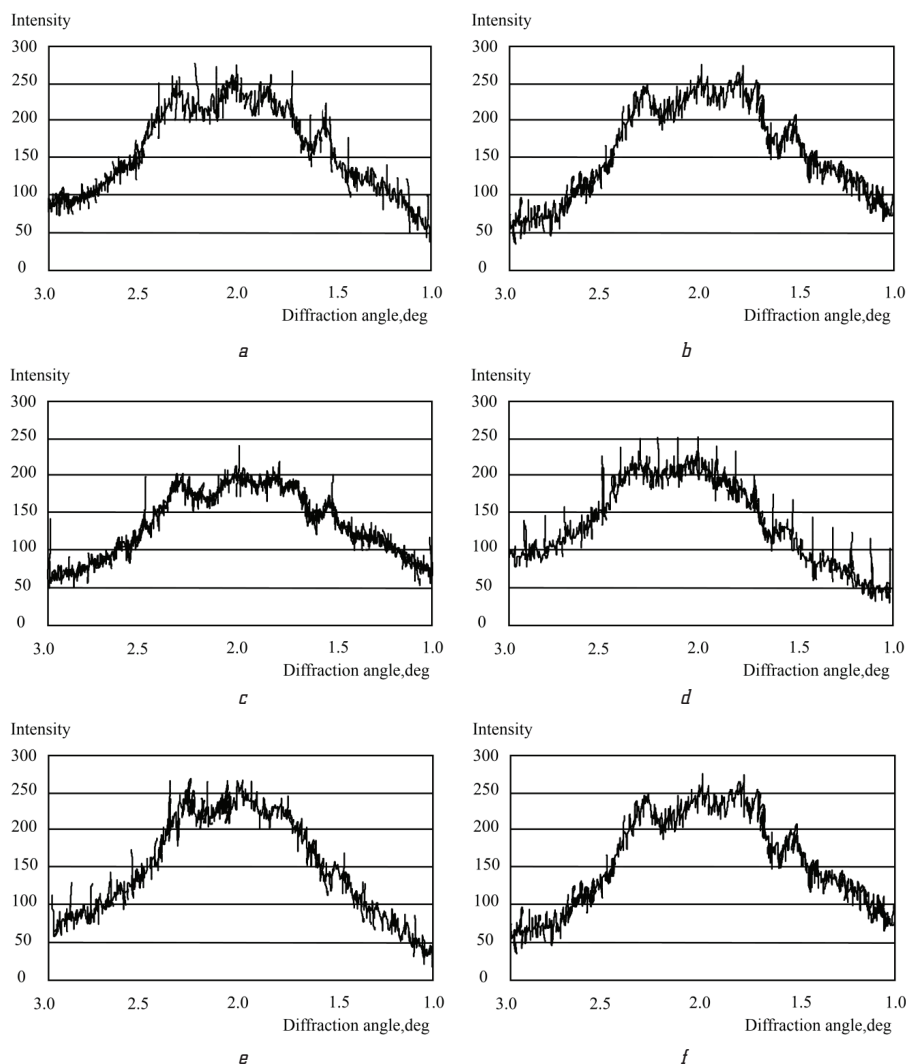


Fig. 3. The diffraction patterns of the control sample of gingerbreads and «Imbyrni Pikantni» gingerbreads:
a – control sample fresh; *b* – control sample after 2 months of storage; *c* – control sample after 4 months of storage;
d – «Imbyrni Pikantni» gingerbreads fresh; *e* – «Imbyrni Pikantni» gingerbreads after 2 months of storage;
f – «Imbyrni Pikantni» gingerbreads after 4 months of storage

After 4 months storage in the control sample, the presence of characteristic maxima of starch is observed, the low intensity of which is explained by the repeated recrystallization of sucrose and starch molecules after loss of moisture by gingerbread cookies. An increase in the intensity of diffraction peaks characteristic of starch in gingerbreads after 4 months of storage is explained by the migration of water molecules from a carbohydrate-bound state to a starch-bound state. Thus, the crystalline structure of starch is restored, and the gingerbread cookies are stale.

4. Conclusions

The use of X-ray phase analysis methods in the work makes it possible to identify the deformation degree of the crystalline structure of starch, that is, to analyze the process of retrograde in the proposed gingerbreads. A study of the author's gingerbread «Bdzhilka» and «Imbyrni Pikantni» is carried out, and the «Pivnichni» gingerbread is selected for the base sample. As a result of studies and comparison of the obtained diffraction patterns of control and developed samples, it is proved that the use of the proposed raw materials slows down the reverse process of starch retrograde. Thanks to the use of rye malt extract, fermented rye malt, artificial and inverted peeled rye flour syrup, the process of staling gingerbreads is inhibited. The research results can be implemented in the confectionery industry in the production of flour confectionery products with the aim of extending the shelf life of these products.

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