Some aspects of the influence of the chemical composition of gel-forming raw materials on the properties of marmalade

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Abstract. This work is aimed at solving the problems of controlling the structural-mechanical, rheological, organoleptic properties of jelly-like confectionery by changing the chemical composition of gel-forming raw materials. The manufacture of jelly marmalade is a complex process owing to the presence of a large number of prescription components that affect the properties of finished products such as sugar, molasses, pectin, modified starch and other structure-forming agents. Since pectin is produced in Russia in small volumes, this limits the possibility of choosing its type due to the high price, which does not always guarantee the stability of the quality of marmalade during storage. Pectin derived from major sources (apple cake, citrus crusts, sugar beet, etc.) differs in chemical properties and molecular chain size. The influence of the composition of carbohydrates on the structural, mechanical and rheological properties has not been adequately studied. Since moisture transfer processes have a significant effect on the shelf life of intermediate moisture products, which include marmalade, it is the chemical composition of the raw material that causes the ratio of bound to free moisture in the marmalade. In the paper the influence of the content of starch syrup (5.0 - 25.0%) on the structural-mechanical (strength) and organoleptic characteristics of model samples of jelly marmalade made on the basis of apple pectin is considered. The obtained patterns can be used to predict the stored capabilities and shelf life of various marmalade items.

1. Introduction

The production of confectionery of the marmalade group is associated with the problems of managing the structural-mechanical, rheological, organoleptic properties by changing the chemical composition of gel-forming raw materials. The manufacture of jelly marmalade is a complex process due to the presence in the recipe of a large number of prescription components that affect the properties of the finished product such as white sugar, molasses, pectin, modified starch and other structure-forming agents. Since pectin is produced in Russia in small quantities, this limits the choice of its type due to the high price, which does not always guarantee the stability of the quality of marmalade during storage.

The structure of jelly marmalade is ensured by the complex of used ingredients including polysaccharide compounds or a mixture of such compounds. Pectin is the most important structure-forming agent, the molecules of which consist mainly of the remainder - 1.4 - D galacturonic acid. Pectin molecules contain homogalacturonan, rhamnogalacturonan I, rhamnogalacturonan II,
xylogalacturonan, apiogalacturonan, arabinan, galactan and arabinogalactan. Depending on the source, pectin may differ in size of molecules, degree of acetylation and methylation, as well as the content of galacturonic acid and neutral sugar residues.

Pectin is produced industrially from apple cake and citrus peel by extraction in the presence of acid, followed by filtration and precipitation with alcohol. The yield of pectin and the content of galacturonic acid vary significantly depending on the source plant [1 - 8].

The content of pectin in apple squeeze and citrus peel is 10.0–16.0% and 20.0–30.0% in terms of dry matter, respectively [9]. Sunflower baskets and sugar beets are also rich in pectin and contain 10.0 - 20.0% pectin in terms of dry matter [10, 11].

The water content in sucrose-based confectionery can vary from 30.0% to 1.0 - 2.0%, and the water activity is from 0.40 to 0.75. For jelly marmalade, this indicator is in the range 0.50 - 0.75, depending on the chemical composition of the components used and the method of technological processing [12].

The content and properties of the main recipe components, including water in the composition of jelly marmalade, are crucial for the quality of the finished product [13, 14]. It is the ratio of free and bound moisture that has a significant effect on texture and shelf life. A high moisture content can cause a “soaking” of the surface, and a low moisture content, on the contrary, leads to the formation of a sugar “crust” on the surface of jelly marmalade.

The results of studies of the influence of the composition of the used raw materials and semi-finished products on the physicochemical and structurally mechanical properties of jelly marmalade are described in a number of works [15, 16]. The most important technological component in the proposed research models of marmalade on pectin is starch syrup as an anti-crystallizer, the content of which determines the value of the strength index of the finished product body.

An important factor affecting the structure of jelly masses is the chemical composition of various types of modified starch [17]. Using a modified starch with desired moisture-retaining and structure-forming properties, you can control the safety of confectionery products made on the basis of gel-forming raw materials.

2. The purpose of the study
The aim of this work was to study the effect of the chemical composition of the raw materials used on the organoleptic characteristics and strength index of jelly marmalade samples. The received regularities are necessary to control the water-holding properties of marmalade to guarantee a specified shelf life.

3. The object of the study
The objects of study were samples of jelly marmalade with a mass fraction of moisture of 22.0%.

The recipe composition of marmalade includes white sugar with a mass fraction of 54.0 - 69.0%, high esterification apple pectin (70.0 - 77.0%) with 65.0% of galacturonic acid, 50.0% of citric acid solution (0.75 - 0.85 cm³), flavor (0.1 - 0.3%)

The obtained samples of jelly marmalade differed in the content of starchy molasses (5.0 - 25.0%). The effect of modified polysaccharides (starches) on strength characteristics and jelly mass formation was also investigated.

4. Materials and methods
Water activity is determined by the method in accordance with GOST ISO 21807 - 2015 “Microbiology of food products and feed. Determination of water activity”, based on the definition of dew point on a device AquaLab (USA) model 3TE.

The pH value of model samples is determined by the method in accordance with GOST 5898 - 87 "Confectionery. Methods for determining acidity and alkalinity”.

Mass fraction of moisture is measured according to GOST 5900 - 2014 "Confectionery. Methods for determining the mass fraction of moisture and solids", accuracy indicator (borders of an absolute
The study of the strength of the samples was carried out on a structure meter ST - 2 (Russia).

Jelly marmalade: sugar – 75.0 - 55.0%, molasses – 5.0 - 25.0%, apple and citrus pectin – 1.0 - 2.5%, sodium citrate salt – 0.2 - 0.3%. The mass fraction of moisture in the finished jelly marmalade on pectin was 22.0 - 22.5%.

5. Discussion of the results

Starches of various names differ greatly in their water-holding ability. In order to compare and predict changes in the water-holding properties and strength of confectionery products made using modified starch, water activity and the strength of a 10% gel based on various types of modified starch were studied (table 1).

Table 1. Physico-chemical properties of 10% gels based on various types of modified starch.

| Type of Modified Starch                      | Water activity, $a_w$ | Strength, g/cm$^2$ |
|----------------------------------------------|-----------------------|--------------------|
| Starch Phosphate (E 1412)                    | 0.982 – 0.988         | 71.5 – 73.0        |
| Acetylated Starch Adipate (E1422)            | 0.971 – 0.978         | 66.0 – 66.8        |
| Acetylated Starch Adipate with pregelatinization (E1422) | 0.986 – 0.992 | 67.0 – 68.5        |
| Hydroxypropyl Starch Phosphate (E1442)       | 0.970 – 0.978         | 59.0 – 62.5        |
| Acetylated Starch Adipate (E1412)            | 0.985 – 0.993         | 68.5 – 71.0        |

Water activity of 10% of gels made using modified starch is in the range from 0.974 to 0.993. Moreover, the strength of the samples studied was 61.0 - 72.0 g/cm$^2$, which makes it possible to produce confectionery products with a wide range of organoleptic properties.

The obtained results of the strength of jelly masses showed that the used concentration of modified starch 10.0% is insufficient for the formation of the structure of jelly marmalade, although the formation of a mass with a jelly-like consistency occurred.

By the ratio of water activity and the strength of the formed gel for further studies substantiated the use of three types of modified starch:
- E1412 with the highest strength and the highest coefficient of thermal stability;
- E1422 with the highest water-holding ability;
- E1442 with acceptable levels of strength and water-holding ability.

Based on these three types of modified starch, marmalade samples are made, which are characterized by various properties.

The results of a study of strength, the mass fraction of moisture and water activity and are presented. The properties of marmalade depend on the content and properties of the modified starch. Marmalade made with the addition of starch E 1442 has optimal strength characteristics.

The influence of the mass fraction of starchy syrup on the physicochemical properties of jelly marmalade made using 1.8% apple pectin with a high degree of methoxylation (71.0%) was studied. The mass fraction of starchy syrup was in the range from 5.0 to 25.0%. The total prescription amount of syrup and white sugar was constant and provided 73.0% (table 2).
Table 2. The influence of the mass fraction of starchy caramel syrup on the physicochemical properties of jelly marmalade on apple pectin

| Mass fraction of starch syrup in jelly marmalade, % | Marmalade indicators |         |
|---------------------------------------------------|----------------------|---------|
|                                                   | water activity (a_w) | Strength, g/cm² |
| 5.0                                               | 0.720                | 380     |
| 10.0                                              | 0.731                | 450     |
| 15.0                                              | 0.754                | 550     |
| 20.0                                              | 0.748                | 530     |
| 25.0                                              | 0.740                | 500     |

Studies have been conducted on the effect of the mass fraction of starch syrup on the properties of jelly marmalade. The mass fraction of moisture in marmalade samples was 22.0%. Water activity was in the range of 0.71 - 0.76.

It is shown that with an increase in the mass fraction of syrup in marmalade to 15%, the plastic strength increases. With a further increase in the mass fraction of syrup to 25%, a decrease in the plastic strength of marmalade mass was revealed.

With an increase in the mass fraction of molasses to 15%, an increase in water activity from 0.72 to 0.76 was revealed, which is probably due to the displacement of moisture associated with pectin and the formation of hydrogen bonds between pectin and molasses carbohydrates. A layer of polar carbohydrate molecules from molasses is formed near the pectin molecules.

With a further increase in the mass fraction of molasses, i.e., with an excess of carbohydrate molecules, the water activity slightly decreases to 0.73 - 0.74, which can be explained by the binding of moisture to molasses carbohydrates. Water molecules bind to the polar groups of glucose, maltose and other carbohydrate molecules in molasses.

The influence of the mass fraction of starch syrup on the physicochemical properties of jelly marmalade made using 1.8% citrus pectin was studied.

Table 3. The influence of the mass fraction of starchy caramel syrup on the physicochemical properties of jelly marmalade based on citrus pectin

| Mass fraction of starch syrup in jelly marmalade, % | Marmalade indicators |         |
|---------------------------------------------------|----------------------|---------|
|                                                   | water activity (a_w) | Strength, g/cm² |
| 5.0                                               | 0.717                | 660     |
| 10.0                                              | 0.728                | 700     |
| 15.0                                              | 0.759                | 960     |
| 20.0                                              | 0.729                | 610     |
| 25.0                                              | 0.729                | 580     |

Jelly marmalade made using citrus pectin is characterized by higher strength compared with marmalade on based apple pectin, which is associated with the technological features of its manufacture (increased amount of citric acid, higher degree of methoxylation).

6. Conclusion
The effect of the amount of starch syrup in the formulation on the strength characteristics and water activity of model samples of jelly marmalade made using highly esterification apple and citrus pectin was studied. The maximum strength of marmalade is achieved using 15.0%
molasses. The highest water activity was also detected using 15.0% molasses, which allows one to predict the highest rate of moisture transfer and the formation of a “crust”. When the amount of molasses is increased to 20.0%, the adhesion and elastic-plastic properties of jelly marmalade increase, which can be used to adjust the shelf life of products of this group. Improving the strength characteristics is accompanied by an increase in water activity, which predicts an increase in the rate of moisture transfer processes and a decrease in the shelf life of jelly marmalade.

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