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Analysis of The Composition and Properties of Structure Stabilizers for Products Based On Dairy Raw Materials.

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ABSTRACT

Were studied the composition and properties of structure stabilizers of products based on dairy raw materials. Each angidropiromnase unit of carboxymethylcellulose (CMC) molecule contains three OH- groups, capable of reacting with monochloracetate sodium. Theoretically there is a possibility of substitution of all three OH-groups (a degree of substitution is equal to three), however, in practice the degree of substitution of CMC is from 0.4 to 1.2. When the degree of substitution is equal to 0.5 and 0.8, the pK values of carboxyl groups are respectively of 4.0 and 4.4. At pH 7.0 about 90% and at pH 5.0 about 10% of carboxyl groups are in a salt form. Carboxymethylcellulose is an ionogenic cellulose ether, therefore, its stabilizing effect depends on salt concentration and other properties of the medium. The most viscosity of equivalent concentrated solutions of CMC was observed at pH from 6 to 8. Most likely, in this pH range takes place the unraveling of macromolecules by the electrostatic repulsion of ionized carboxyl groups. At low pH values is observed a suppression of ionization of carboxylic groups in acid form, and at high pH values the repulsive forces are reduced due to the presence of a large number of sodium ions. It follows from the above that at extreme pH levels the macromolecule of carboxymethylcellulose is minimized and in the optimal pH range from 6 to 9 it is straightened.

Keywords: carboxymethylcellulose, milk, stabilizer, microstructure.

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INTRODUCTION

Development of modern technological principles of food production is associated with the search for universal ways of influencing the multicomponent aqueous systems; one of them is the use of food structure stabilizers [1]. The approaches for their use are in their mixing with food products with the subsequent transfer of the aqueous phase of the system in the gel state [2]. Among the currently known structure stabilizers are widely used the anionic polysaccharides, both of the natural (pectin, agar, agaroid, pyrophosphate) and artificial (oxidized starch) origin [3]. The alginates, cellulose derivatives, carboxymethylcellulose (CMC), and various gums [4] are wide spread abroad.

One of the classic stabilizers of the structure is agar, which has been widely used in the confectionery industry. However, the growing shortage of source of agar necessitated its replacement with the other stabilizers of the structure [5]. For example, one of the most promising stabilizers of the structure could be a various kind of pectin [6]. Currently they are used in food and pharmaceutical industries [7]. Pectins are capable of forming gel systems characterized by a specific set of physico-chemical properties [8]. Moreover, it was found that pectin has a beneficial effect on the human body, and resources for the production of pectin are almost unlimited [9, 10].

MATERIALS AND METHODS

At different stages of the research the experimental objects were: cow's raw milk of a second grade and higher according to State standard - GOST 13264; cream, obtained by separation of cow's milk (GOST R 52054); skim cow's milk, without foreign tastes and odors, with the acidity not more than 20°T, obtained by separation of cow's raw milk of the appropriate grade; skimmed milk powder (GOST 10970); lyophilized culture of a direct adding FD-DVS CH-N-19 (consisted of *Lactococcus lactis spb. cremoris, Lactococcus lactis spb. lactis, Leuconostoc mesenteroidis spb. cremoris, Lactococcus lactis spb. lactis biovar diacetylactis*) и EZAL U-D MYE 96 (consisted of *Streptococcus termophilus, Lactobacterium delbrueckii spb. bulgaricus*); starter cultures of a direct application, specially developed for the Russian market a series of "DELVO-YOG", hard cheese, semi-hard, soft and brine according to the current normative-technical documentation; cheeses, and masses of cheese for melting according to the standard TU 9225-113-04610209; low-fat cheeses for melting according to the standard TU 9225-107-04610209; cheese mass for melting according to the standard TU 9225-113-04610209; the mass of cheese for melting according to the standard TU 9220-001-83196489; stabilizers of the structure of the following types: CMC Akucell 3265; CMC 4500-6000; konjac guma; CMC 6000-9000; pectin ARA 105; carob guma; sodium alginate HO4-600; sodium pyrophosphate SAPP 28; the CMC Akucell 2785; sodium pyrophosphate SAPP 40; ksanthano guma; drinking water according to the State standard GOST 2874; flavourings natural or identical to natural, aromatic food essences, essential oil, domestic or imported, approved for use by the Rospotrebnadzor (Russian consumer supervision) of the Russian Federation; sorbic acid according to the standard TU 6-14-358 and TU 6-14-22-206; nisin according to the current normative documents, was received to import, and is permitted for use by the Rospotrebnadzor of the Russian Federation; amendments (stabilisers): carrageenan, carob guma, guar guma, ksanthan guma, di-starch-phosphate and (or) modified starches domestic or imported, and the production of “BK Giulini”, Germany ("Turrisin", "Becaplus"), authorized for use by the Rospotrebnadzor of the Russian Federation; potato starch modified domestic or imported) allowed for use by the Rospotrebnadzor of the Russian Federation, the other auxiliary raw materials, and materials that meet the requirements of current normative and technical documentation.

In carrying out the work were using conventional, standard and original methods.

Selection of milk and dairy products, preparation for analysis were made according to GOST 26809-86. Sampling for microbiological studies was made according to GOST 9225-84.

Mass fraction of macroelements and microelements was determined by the atomic absorption spectrophotometry. The principle of the method is based on the ability of dissociated atoms of elements absorb light in a narrow spectral region. The study was carried out on the device Hitachi (Japan) according to the enclosed instructions. Microbiological parameters were determined taking into account the requirements specified in SanPiN 2.3.2.1078-01, on the standard and accepted methods, taking into account the requirements specified in MU 4.2.727-99 "Hygienic assessment of shelf life of food products": bacteria of

intestinal sticks group (E. coli), the number of mesophilic aerobic and facultative anaerobic microorganisms according to GOST 9225; pathogenic microorganisms, including bacteria of the Salmonella genus,- GOST 30519, GOST R 50480; Staphylococcus aureus according to GOST 30347; mold and yeast according to GOST 10444.12.

A total protein analysis is conducted using Duma`s method, and is based on the measurement of thermal conductivity of molecular nitrogen, that is formed upon combustion of the test sample at a temperature of about 1000º C in an oxygen atmosphere with the subsequent recovery of all the resulting nitrogen oxides with a reducing agent (copper), with using of the protein nitrogen analyzer RAPID N Cube (Elementar, Germany). The determination process is fully automated. At the stage of a sample preparation the sample is tableted using a foil that is not containing nitrogen. The weighed sample is 250 mg. To obtain reliable results were carried out three - five parallel analyses of each sample.

Determination of the mass content of water-soluble vitamins and inorganic anions was carried out by capillary zonal electrophoresis using the system of capillary electrophoresis "Capel 105". The method is based on the migration and separation of the ionic forms of analyzed components under the influence of an electric field due to different electrophoretic mobility, with the subsequent registration.

Determination of content of toxic elements, pesticides, antibiotics and radionuclides: lead – according to GOST R 51301, GOST 26932 and GOST 30178, GOST 30538 and MUK (methodical instructions) 4.1.986; arsenic – GOST R 51766, GOST 26930 and GOST 30538; cadmium – according to GOST R 51301, GOST 26933, GOST 30178, GOST 30538 and MUK 4.1.986; mercury – GOST 26927 and MU 5178; residual quantities of organic chlorine pesticides – according to GOST 23452 and MU 6129; aldrin – on methods for determination of trace amounts of pesticides in food, feed and the environment; antibiotic - MU 3049, MR 4.18/1890, MUK 4.2.026; radionuclides strontium-90 and cesium-137 – MUK 2.6.1.1194.

Titratable acidity according to GOST 3524-92. The method is based on neutralization of acids and their salts contained in the product by the solution of caustic alkali in the presence of phenolphthalein indicator. Active acidity was measured on the potentiometric analyzer according to GOST 26781-85.

Evaluation of taste and smell according to GOST 28283-92.

Determination of moisture content and dry matter according to GOST 3626.

The total protein content according to GOST 23327-78.

Mass fraction of sucrose was determined by iodometric titration according to GOST 3628 (arbitration method). The method is based on oxidation of reducing sugars containing aldehyde group with iodine in an alkaline environment. Mass fraction of sucrose was calculated by the difference between the taken amount and the amount of unspent iodine, determined by the titration.

In the study were used modern instrumental, physical, physico-chemical and rheological methods. Below are the basics of the research methods used in the work, which received the most essential characteristics of a structured cheese product.

RESULTS AND A DISCUSSION

The fig. 1 shows micrographs of CMC Akucell 3265 at a magnification of 100, 200 and 500 times.

From the obtained microphotographs, shown in Fig. 1, it is seen that the structure of the CMC Akucell 3265 consists of dispersed elements that are presented in the form of elongated fibers with a rough surface, whose diameter is around of 20-30 microns. The CMC Akucell 3265 is characterized by the lowest bulk density of all tested stabilizers of the structure that is 450 g/dm^3.

CMC is a salt of a weak carboxylic acid, obtained by the interaction of monochloracetate sodium with alkaline cellulose.

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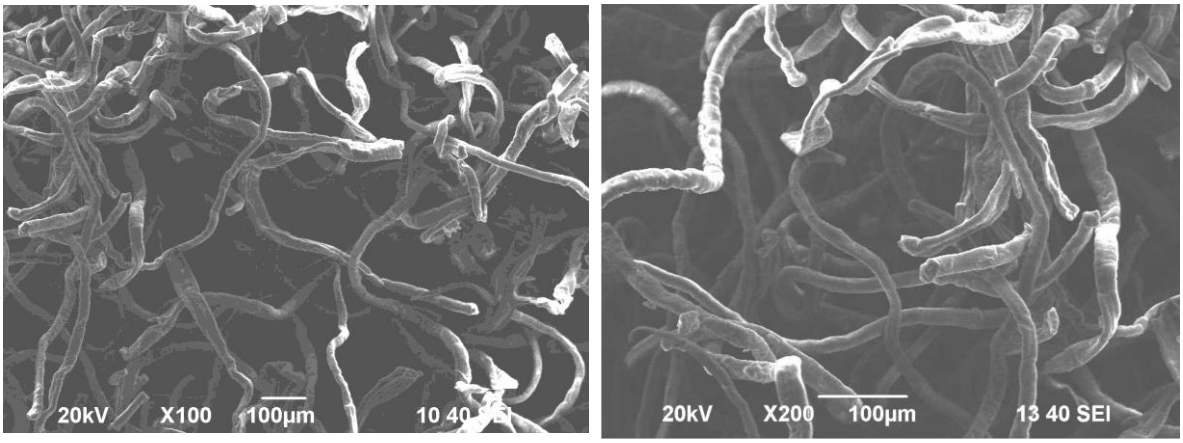

Fig. 1. The microstructure of the CMC Akucell 3265 at a magnification: a – in 100 times; b – in 200 times; c – in 500 times

To obtain this type of the structure stabilizer the α-cellulose obtained from plant fibers is processed in strongly alkaline solution and chloroacetic acid, and the resulting sodium chloride is washed. Carboxymethylcellulose contains such substances as the food salt (NaCl), sodium glycolate and unsubstituted cellulose.

Each of the angidropyronase units of molecule of carboxymethylcellulose contains three OH-groups, capable of reacting with monochloracetate sodium. Theoretically there is a possibility of substitution of all three OH-groups (a degree of substitution is equal to three), but in practice the degree of substitution of CMC is from 0.4 to 1.2. When the degree of substitution is equal to 0.5 and 0.8, the pK values of carboxyl groups consist of 4.0 and 4.4 respectively. At pH 7.0 about 90% and at pH 5.0 about 10% of carboxyl groups are in a salt form. Carboxymethylcellulose is an ionogenic cellulose ether, therefore, its stabilizing effect depends on salt concentration and other properties of the medium. The most viscosity of the equivalent concentrated solutions of CMC was observed at pH from 6 to 8.

Most likely, that in this pH range takes place the unraveling of macromolecules by electrostatic repulsion of ionized carboxyl groups. At low pH values is observed a suppression of ionization of carboxylic groups in acid form, and at high pH values the repulsive forces are reduced due to the presence of a large number of sodium ions. It follows from the above that at extreme pH levels the macromolecule of carboxymethylcellulose is minimized, and in the optimal range of pH from 6 to 9 it is straightened (Fig. 2).

The chain length, degree of substitution and neutralization influence for the solubility and technological properties of CMC. So, in the presence of 1% of CMC in a water solution its viscosity varies from 20 to 3500 PA•s. CMC is good soluble in water and alkali, slightly soluble in glycerol and acids and almost insoluble in organic solvents. The solubility of CMC can be improved through the use of more active solvents, one of which is a diluted solution of caustic soda, which allows to increase the degree of substitution to values close to 1.2 (Fig. 3).

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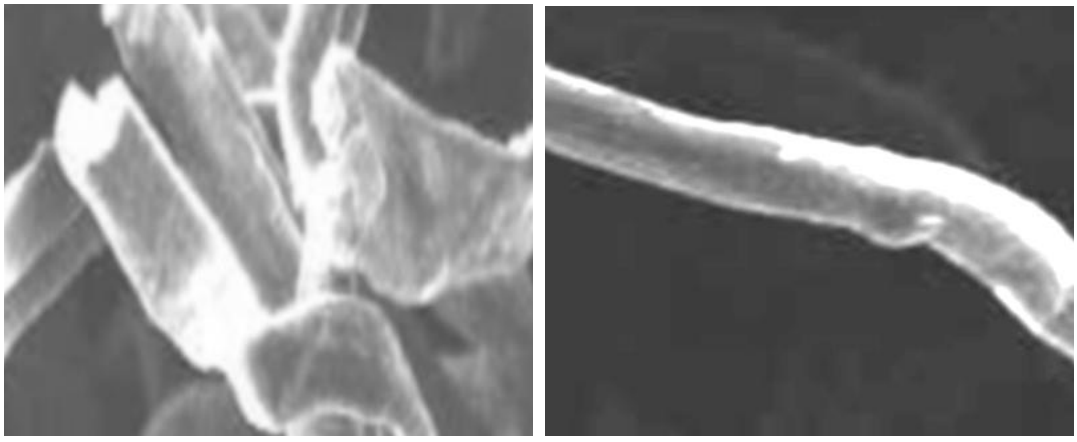

a b

Fig. 2. Macromolecule of CMC in the minimized (a) and straightened form (b), a magnification of 5000 times.

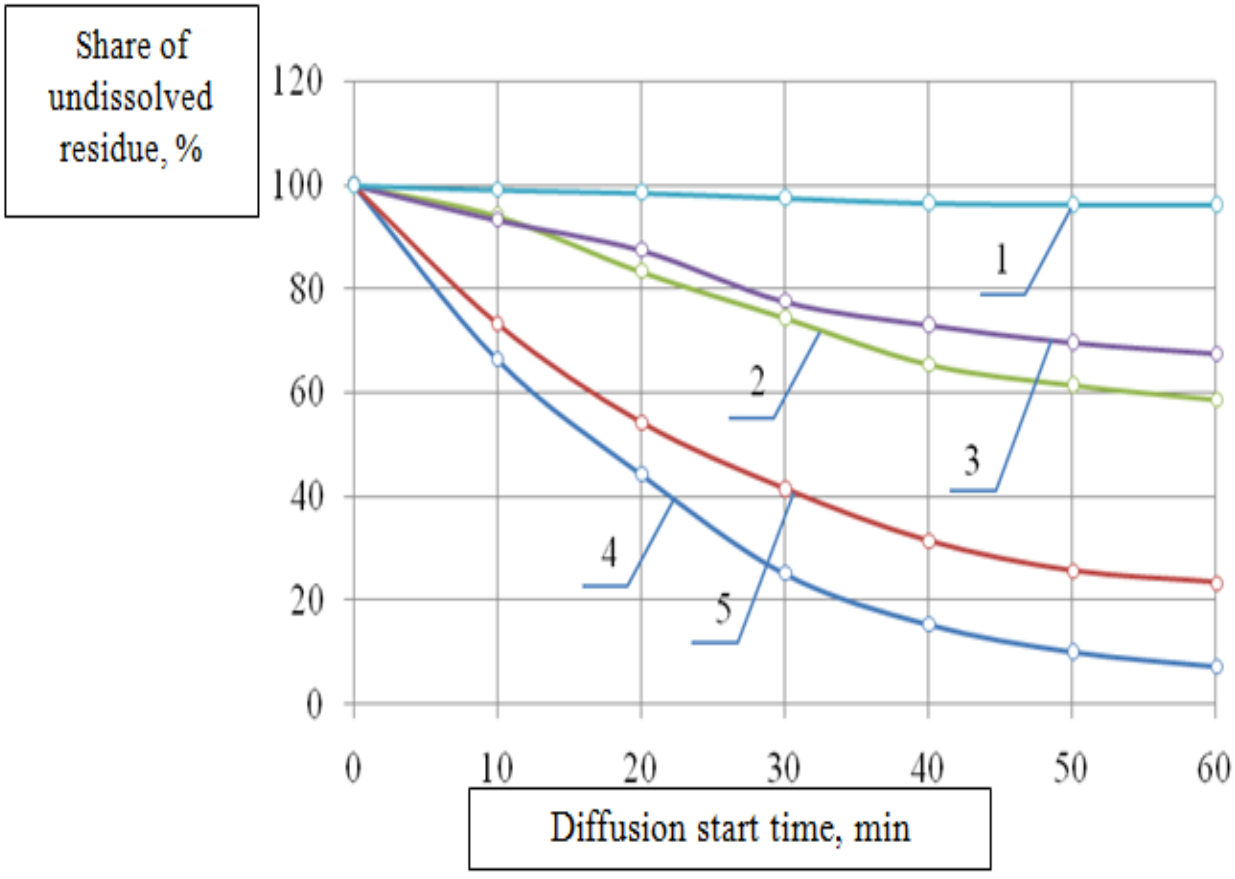

Fig. 3. The dependence of the undissolved residue of CMC on the duration of processing: 1 – in organic solvents; 2 – in acids; 3 – in glycerol; 4 – in water; 5 – in leach.

Fig. 4 shows the spectrometric profile of the composition of the CMC Akucell 3265. The three characteristic peaks are in the resulting profile, corresponding to carbon, oxygen and sodium and two shallow sites, corresponding to nitrogen and chlorine. Table 1 shows the component composition of the CMC Akucell 3265.

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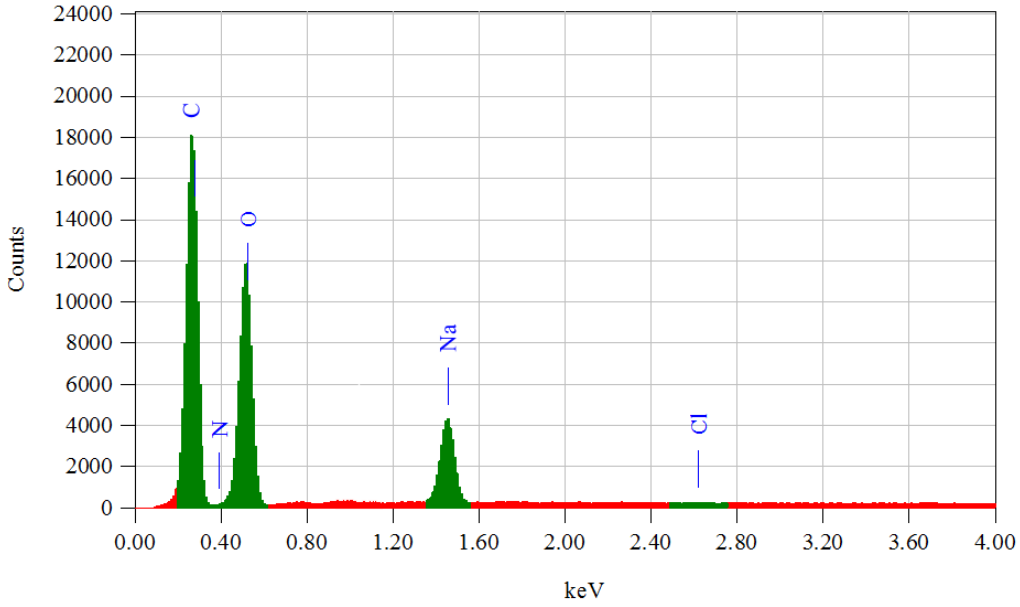


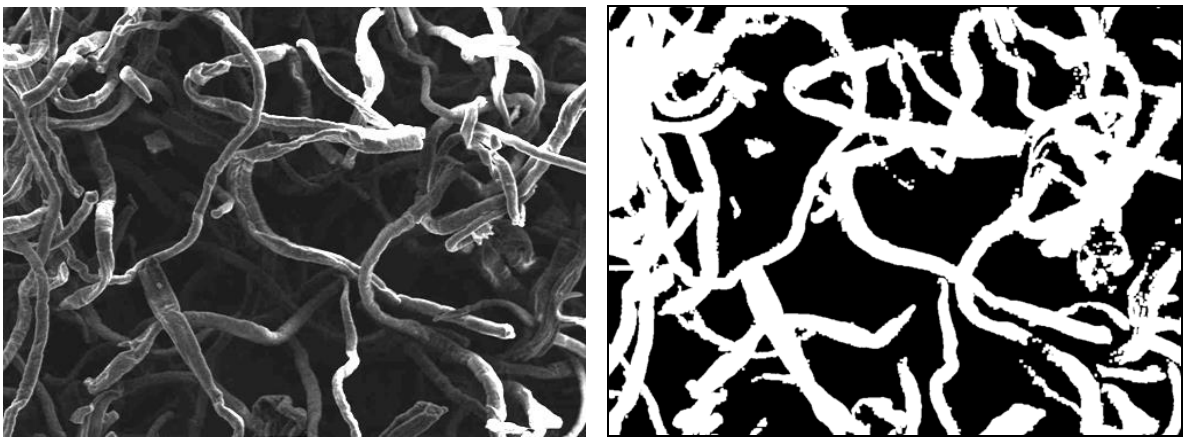
Fig. 4. The spectrometric profile of the composition of the CMC Akucell 3265

From the presented results it follows that in the CMC Akucell 3265 an oxygen is dominating (42,78%). The chlorine is characterized by the lowest concentration (0,07%).

Table 1: The component composition of the CMC Akucell 3265

Element	The relative weight, %
Carbon	31,15±0,93
Nitrogen	21,90±0,65
Oxygen	42,78±1,28
Sodium	4,01±0,12
Chlorine	0,07±0,002

To determine the micro hollows in the CMC Akucell 3265 was used a microphotograph shown in Fig. 5 (a). In this case there was a need in a filtration of the elements presented in the background by increasing of the contrast and by a manual correction of the mask. The results of the determination of micro hollows in the CMC Akucell 3265 are shown in Fig.5.



a b

Fig. 5. The results of determining the fraction of micro hollows of CMC Akucell 3265: a - microphotograph with a magnification of 100 times; b - mask of the micrograph shown in Fig. (a)

According to the results of histogram a desired content of micro hollows in the CMC Akucell 3265 was 51,24±2,2%.

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INSIGHTS

Thus, the microstructure of the CMC Akucell 3265 is characterized by a low bulk density of 450 g/dm3, its elements are presented in the form of elongated fibers with a diameter of 20-30 microns. In the chemical composition of the CMC Akucell 3265 there are such elements as carbon, nitrogen, oxygen, sodium and chlorine. The content of micro hollows in the investigated structure stabilizers was 51,24±2,2%.

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