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The Effect of Sugar Substitutes on Structure Formation in the System of Agar and Helianthus Tuberosus Pulp

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Abstract: Peculiarities of structure formation of agar in the presence of Helianthus Tuberosus (Jerusalem artichoke) pulp were studied using methods for determining gel strength, IR spectroscopy and viscometry. It was established that introduction of Helianthus Tuberosus pulp increases the strength of agar gels by decreasing its critical concentration of structure formation. The mechanism of structure formation was determined. It was shown that H-bonds between -OH and -COOH groups of macromolecules of agarose and D-galacturonic acid of pectins in the content of Helianthus Tuberosus pulp, stabilized by hydrophobic interactions of their nonpolar parts, are responsible for structure formation in the system. The effect of sugar substitutes and citric acid on the strength of obtained agar and Helianthus Tuberosus pulp gels was studied. It was established that the increase of stevioside and sorbitol concentrations leads to increase of system strength, caused by formation of H-bonds between molecules of agarose, pectin and sugar substitutes. The effect of citric acid on structure formation is favorable only at low concentrations (<3%), at concentrations of more than 3%, strength starts to decrease due to hydrotropic action of citric acid molecules.

Key words: Agar · Helianthus tuberosus (Jerusalem artichoke) · Structure formation

INTRODUCTION

Currently, of particular relevance is the problem of development of anti-aging solutions. One way of solving this problem is the creation of food products with a minimum amount of synthetic ingredients. Such products include structured food systems [1, 2, 3, 4].

Among food products structured systems are of particular importance. For their production, such fast structuring polymers as gelatin, agar, starch and carrageenan, are used. Each of these biopolymers exhibits its own structuring characteristics according to their nature, chemical composition and functional groups. Along with them, fruit systems also have structuring ability and based on that are used in preparation of such confectionery products, as jellies, jams, candy, etc. [1, 2]. The advantage of using them is in abundance of vitamins and other beneficial ingredients that are resistant to the effect of preservatives. However, when used for special-purpose products, it is important to pay attention to the content of sugars. In particular, in production of confectionery products of antidiabetic purpose, preference is given to the fruits containing fructose as the main carbohydrate. Of great interest among researchers is the use of the pulp of Jerusalem artichoke tuberosus, which contains inulin, a natural analogue of insulin [3, 4]. It is proposed to use it as a dietary supplement with a low glycemic index [4]. Probably, by combination of biopolymers and pulp of Jerusalem artichoke, structured systems, which could serve as the basis of food gels of anti-diabetic purposes, can be obtained. In this regard, the aim of this study was to study the effect of sugar substitutes, sorbitol and stevioside, on structuring of agar and pulp of Jerusalem artichoke.

MATERIALS AND METHODS

Materials Agar: Agar (Sigma-Aldrich, USA) was used as the main structurant. Agar is a biopolymer widely used in food technologies, it is derived from marine algae.

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The main fraction of agar is neutral polysaccharide agarose, which forms a solid gel and the second fraction is charged polymer agaropectin, which gives weak gels [5]. Agarose is a linear polymer of agarobiose, a disaccharide composed of β-D-galactopyranose and 3, 6-anhydro-α-L-galactopyranose, connected by 1, 4-bond [6, 7].

Jerusalem Artichoke: Tubers of Jerusalem artichoke tuberosus, grown in Kazakhstan, were used in study. The tubers were cleaned from the skin, cut into cubic particles with the size of the edge of 1.0 cm and then blended in a food mixer (Philips, Netherlands). The resulting pulp was used for structuring with agar.

Chemical composition of Jerusalem artichoke varies depending on the biological characteristics of cultivar and soil and climatic conditions, including agrotechnics, growing conditions and geography. The solids content in Jerusalem artichoke varies: 22.0 - 32.0% in terrestrial mass, 19.0 – 30.0 % in tubers [8].

The Jerusalem artichoke contains a unique carbohydrate complex based on fructose and its polymers, the higher homologue of which is inulin, the most valuable and quantitatively predominant carbohydrate component. It is contained predominantly in tubers of Jerusalem artichoke along with sugars (from 13.0 to about 20.0% of crude weight). The chemical composition of the carbohydrate complex of Jerusalem artichoke tubers (depending on cultivar, growing and storage conditions) per crude weight (%): 11.0-21.0 for inulin; 0.1-0.4 for starch; 1.0-3.0 for hemicellulose; 1.1-3.0 for cellulose; and 0.1-2.5 for mannose [9].

Food Additives Sugar Substitutes Sorbitol: (Medical Union Pharmaceuticals, Egypt) and stevioside (A&Z Food Additives Co., Ltd, China) were used as sweeteners. Sorbitol is used in the production of confectionery and diabetic products. It is non-toxic and absolutely harmless to the organism [2].

Stevioside is also used in the food industry (food additive Å960). It is isolated from the stevia plant (Stevia rebaudiana bertoni) [10, 11]. Complex of sweet substances of stevia consists of eight components, differing from each other by degree of sweetness and quantitative content in the leaves. According to chemical structure, sweet substances of stevia are classified as tetracyclic diterpenoid glycosides, the aglycone of which, steviol, is tasteless. Enzymatic hydrolysis of stevioside leads to the formation of 3 moles of D-glucose and 1 mole of tasteless aglycone of steviol. In acid hydrolysis of stevioside D-glucose and aglyconeisosteviol are formed. Structure of steviol is similar to the structure of steroid hormones and has weak antiandrogenic activity [12, 13]. Citric acid was used for regulating taste and acidity of food gels.

Preparation of Food Gels: For preparation of food gels, 10 g of agar was dissolved in 100 mL of distilled water at 100°C. 10 mL of the resulting solution was mixed with 10 g of the crushed mass of the Jerusalem artichoke, the mixture was stirred and boiled at 120-130°C for 5-7 min. Sweetener and citric acid were injected to the mixture and then incubated for 24 h at 25°C.

Method of Determining the Gel Strength: Determination of the gel strength was conducted on the Weiler-Rehbinder device. The principle of the method is to measure the forces required to displace a plate, immersed in a structured system, for its vertical displacement. For structuring, corrugated plate was inserted into obtained mixture of agar solution and pulp of Jerusalem artichoke. After conditioning for 24 h at 25°C, the force required to eject the plate from the gel was measured. The strength or maximal displace stress was calculated as the ratio of the force required for displace, to twice area of the plate.

Viscometry: Relative viscosities of agar solutions were determined using Ubbelohde viscometer. The method is based on measuring the time for which a certain volume of liquid flows through the capillary of viscometer and comparing it with the flow time of the solvent (water). The measurements were performed in a thermostat at 25°C.

Determination of the Gel Softening Temperature: To determine the softening temperature of the gels, mixtures of agar solution with appropriate additives were prepared. These mixtures were filled in capillaries with 1 mm diameter, sealed on one side and left for 24 h for complete hardening of the gel. Then the capillary with hardened gel was attached to a thermometer and immersed in a flask with water that was heated on a water bath. The temperature, at which the first bubbles appear in the capillary, is considered to be the softening temperature of the gel.

IR Spectroscopy: Infrared spectra of samples of the gels were obtained using Spectrum-65 Fourier IR spectrometer in KBr pellets.

RESULTS AND DISCUSSION

Changing the strength of the gels by introduction of various additives in biopolymers is an effective way of lowering their cost and regulating structural-mechanical properties. In this regard, there is a need to define the effect of various low and high molecular compounds on structuring of agar and determining the mechanism of interaction of structuring components.

The inclusion of Jerusalem artichoke pulp in food gels is a promising approach, since it is rich in natural analogue of insulin, inulin. For this reason, it is recommended for patients with diabetes. In addition, during storage, part of inulin turns into fructose, which replaces sugar in the diet of patients with diabetes [14, 8].

For studying the effect of Jerusalem artichoke pulp on the structuring of agar, experiments on structuring of the biopolymer in an aqueous medium and in the mixture with Jerusalem artichoke pulp were conducted. Agar provides quite stable structures even at 1.5% content, critical concentration of structuring (CCS) is 0.50 % (Fig. 1). Introduction of Jerusalem artichoke into the system shifts the structuring curve to the left, which indicates the increase of polymer structuring and strength. CCS of the system is reduced to 0.30 %.

The basis of the agar is a disaccharide, agarose, which consists of molecules of D-galactose (esterified with sulfuric acid) and 3, 6-anhydro-α-galactose [15]. One of the components of Jerusalem artichoke are pectins. Pectins are linear polymers of D-galacturonic acid, in which part of carboxyl groups are replaced by methanol [16]. In this case, the main type of interactions in the system of agar and Jerusalem artichoke pulp are proposedly hydrogen bonds between OH, COOH groups of pectins and OH groups of agar, as well as hydrophobic interactions between their non-polar parts.

As can be seen from Fig. 1, even at the low content of agar (1.5-2.0%), the gel has sufficiently strong structure. The effect of Jerusalem artichoke pulp on the strength of agar gels is shown better by the data presented in Fig. 2. The introduction of Jerusalem artichoke into the system first increases the strength and then reduces it. The structuring effect on the biopolymer can be associated with the presence of components, that are tend to structuring (proteins, carbohydrates), in the composition of artichoke pulp [17]. In addition, the high content of ions of calcium, magnesium and iron can lead to crosslinking of macromolecules of pectin and agarose.

The decrease in strength of formed gels when the content of Jerusalem artichoke pulp is more than 25% may be caused by dilution of the system due to the prevalence of water in the composition of Jerusalem artichoke (66.0 %). However, the strength decrease is not significant and in the 25-50% range of Jerusalem artichoke pulp concentration, gel strength remains quite high.

For studying the mechanism of interaction of Jerusalem artichoke pulp components with agar, IR spectroscopic analyses were performed (Fig. 3).

In the spectra of agar, peaks in the region from 3400 cm^{-1} to 1632 cm^{-1}, corresponding to hydroxyl group and peak at 2929 cm^{-1}, corresponding to valent vibrations of C-H bonds are observed. This region of IR spectra has a similar appearance for Jerusalem artichoke pulp and its mixture with agar, too. This is similarities take place due to the same basic components of all of these systems, carbohydrates. However, in the mixture, the peak at 3400 cm^{-1}, corresponding to O-H groups, becomes slightly narrower. It should be noted that, N-H bonds in proteins can also influence the intensity of this peak in Jerusalem artichoke pulp and its mixture with agar. Furthermore, peaks corresponding to C-H groups, detected at 2929 cm^{-1} in the agar and at 2936 cm^{-1} in the pulp of Jerusalem artichoke, in their mixtures is displaced to 2938 cm-1, increasing its intensity. These results can indicate formation of hydrogen bonds and hydrophobic interactions in the system.

Peaks in the frequency range of 1632 - 1643 cm^{-1} in the agar and the Jerusalem artichoke in the mixture displaced and increased in intensity to a united absorption band (1643 cm^{-1}). These peaks can be assigned to vibrations involving C=O groups. Moreover, significant changes occur in the peaks in the region of 1156-1072 cm^{-1}, corresponding to vibrations of a polar connection of C-O. This may indicate participation of carboxyl groups in the formation of hydrogen bonds. The role of carboxyl groups in the structuring is twofold: they can participate in the formation of H-bonds, contributing to the structuring; and when dissociated, may undergo electrostatic repulsion, which is not favorable for structuring.

Significant difference is observed in the right part of the IR spectra. In the agar, several peaks appear in the interval of 800-700 cm^{-1}, which can be attributed to $–OSO_3$ or OH groups. In the spectra of Jerusalem artichoke pulp, multiple peaks are also observed in this region, which can be caused by the presence of OH-groups, as well as the presence of cations (Fe^{3+}, Ca^{2+} and Mg^{2+}). In the mixture of biopolymer and Jerusalem artichoke, changes in intensity and width of the peaks take place, as well as peaks displace. It is suggested, that this phenomena is caused by participation of metal ions in the ion exchange reactions, which defines their crosslinking action on the molecules of agarose and pectins, as well as the formation of H-bonds.

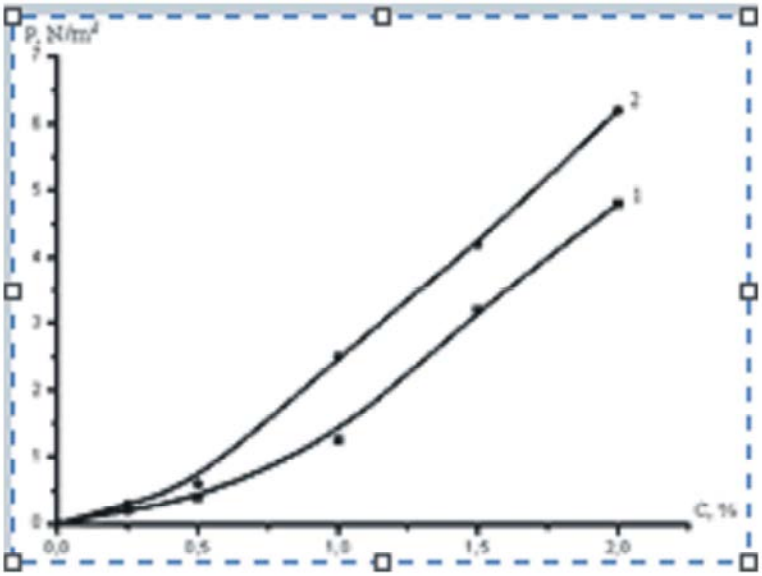

Fig. 1: Dependence of the gel strength on concentration of agar: 1 – agar; 2 – agar and Jerusalem artichoke pulp (20%)

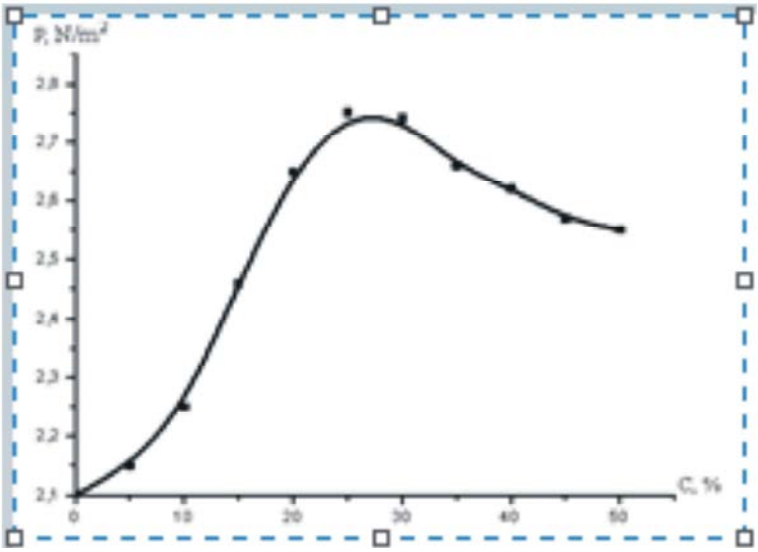

Fig. 2: Dependence of the agar and Jerusalem artichoke pulp gel strength on the content of Jerusalem artichoke: (C_{agar} = 1.0 %)

Thus, structuring in the agar and Jerusalem artichoke pulp system may be provided by the formation of H-bonds between OH, COOH-groups of agarose and pectins, stabilized by hydrophobic interactions between their nonpolar parts and crosslinking action of Fe^{3+}, Ca^{2+} and Mg^{2+} ions in the composition of the Jerusalem artichoke pulp.

The presence of sugars in confectionery jelly products, besides giving them a sweet taste, has a preservative action on the system. However, in order to fight the increase of glucose level in the blood, substitutes of sugar are used. The most widely used sweeteners are fructose, xylitol, sorbitol, aspartame, saccharin, sodium cyclamate, potassium acesulfame, sucralose, stevioside [18]. From such a wide range of sugar substitutes, sorbitol and stevioside were used in the study. These substitutes were chosen is due to the absence of contraindications to their use in the literature. Results of experiments on the structuring of agar in the presence of sugar substitutes are shown in Fig. 4.

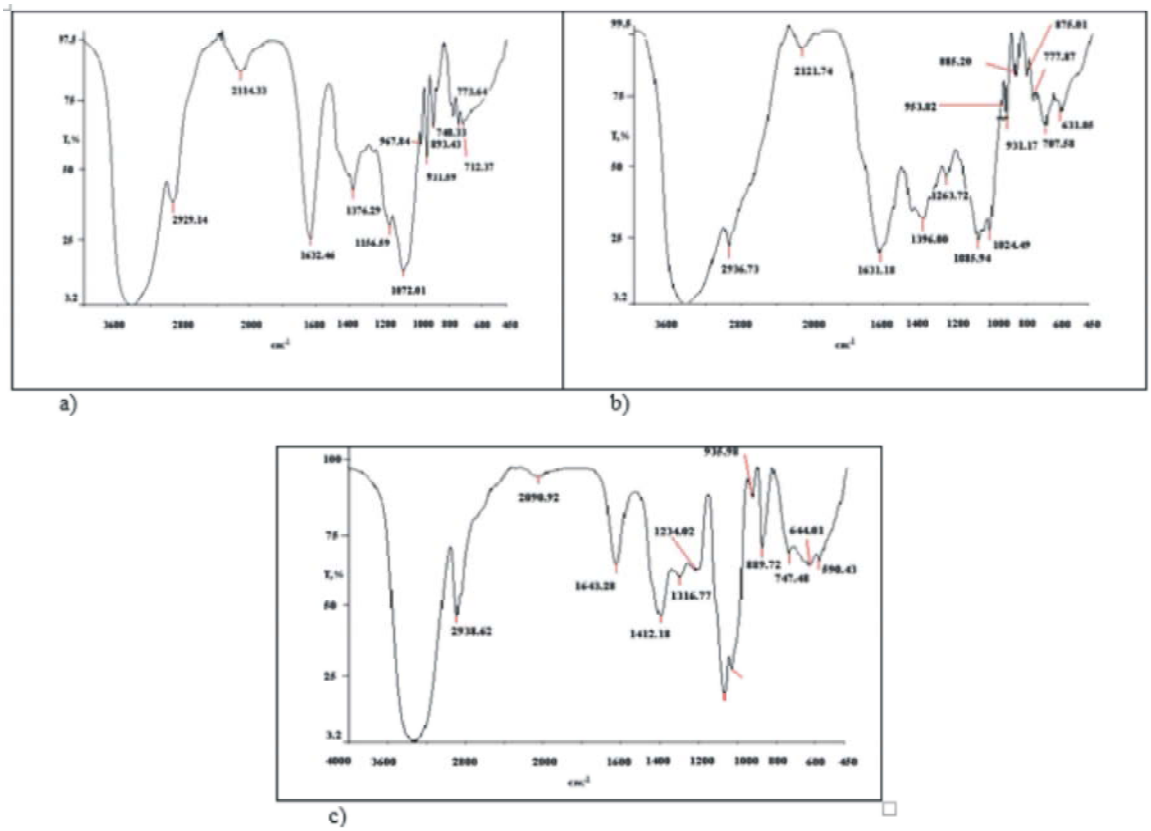

Fig. 3: IR spectra of agar (a), pulp of Jerusalem artichoke (b) and agar and Jerusalem artichoke pulp system (c)

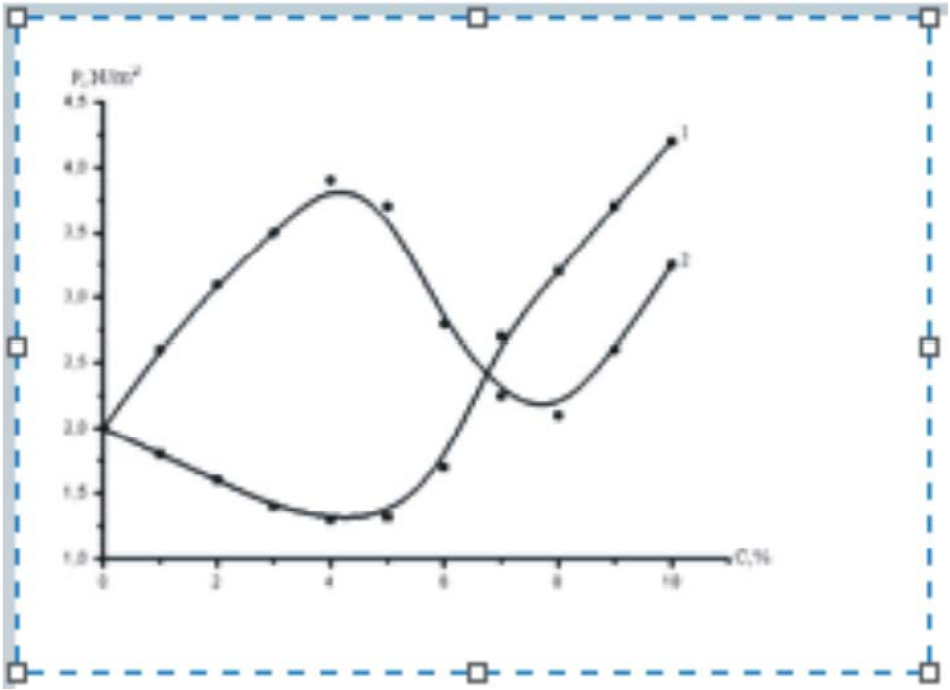

Fig. 4: Effect of sugar substitutes content on the strength of the agar and Jerusalem artichoke pulp gels: (C_{agar} = 1.0 %, CJA = 20 %, T = 25°C); 1 – stevioside; 2 – sorbitol

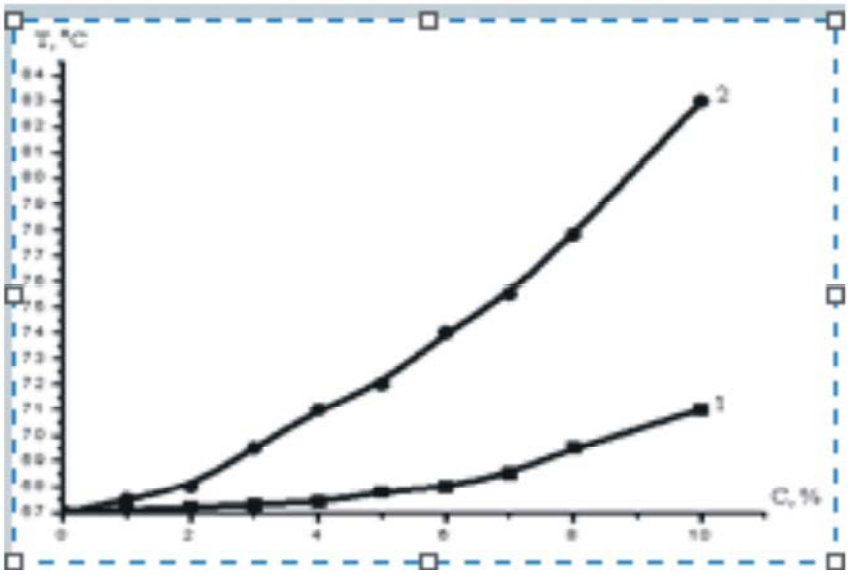

Fig. 5: Effect of sugar substitutes concentration on the softening temperature of the agar and Jerusalem artichoke gels: (C_{agar} = 1.0 %, CJA = 20 %); 1 – stevioside; 2 – sorbitol

At 1-5% content, stevioside gives fragile structures, however, with the increase of its concentration above 5%, the gel strength increases. Stevioside is a tetracyclic glycoside, thus the main probable type of interactions in the system are H-bonds between OH-groups of glycoside molecules and macromolecules of agar, as well as hydrophobic interactions between their non-polar parts.

Sorbitol behaves differently, forming strong structures at low concentrations (1-5 %). At higher concentrations of sorbitol, gel strength decreases and then the strength increases again. These changes in the strength of gels can be caused by competitive interactions between the ingredients of the food system, capable of formation of H-bonds and hydrophobic interactions.

Beneficial effect of sugar substitutes on the structuring of the system is also observed in the increase in the softening temperature of agar with addition of sorbitol and stevioside (Fig. 5). However, in contrast to the values of strength, in the data of measuring the softening temperature of gels no abrupt changes are observed. On the other hand, such monotonous increase in the softening temperature of food gels testifies the stability of the gels to storage.

Some information about the structure formation in polymer systems can be obtained from the viscometry data. The peculiarity of this method is the need to use dilute solutions of polymers, as the polymer solutions with high concentrations begin structuring during the study experiments. Thus, agar solutions with concentration of 0.02 % were used. Fig. 6 describes the dependence of the relative viscosity of agar and sugar substitutes system on the concentration of sugar substitutes.

As can be seen from the figure, at low concentrations of sugar substitutes, a sharp decrease of relative viscosity of the polymer solution occurs. However, further increase in the concentration of stevioside and sorbitol leads to increase of relative viscosity. The decrease of relative viscosity at low concentration of sugar substitutes may be caused by compression of the polymer chain as a result of interaction of the molecules of sugar substitutes with agarose due to hydrogen bonds, stabilized by hydrophobic interactions between their non-polar parts. As a result, the biopolymer macromolecule is twisted, which leads to decrease of its size and, consequently, to decrease of relative viscosity of solution. The introduction of additional quantities of sugar substitutes into this system leads to an enrichment of the polymer chain with OH groups, prone to hydration. This results in the unfolding of macromolecules of the biopolymer and, consequently, value of relative viscosity increases. Curve $\eta=f(c)$ for the agar and sorbitol system is higher than the corresponding curve for the agar and stevioside system, which can be caused by the higher content of OH-groups in a hexahydric alcohol, sorbitol. Based on the foregoing, we can conclude that the presence of stevioside and sorbitol is favorable for the structuring of agar. By introducing sugar substitutes, it is possible to adjust the strength of the food gel.

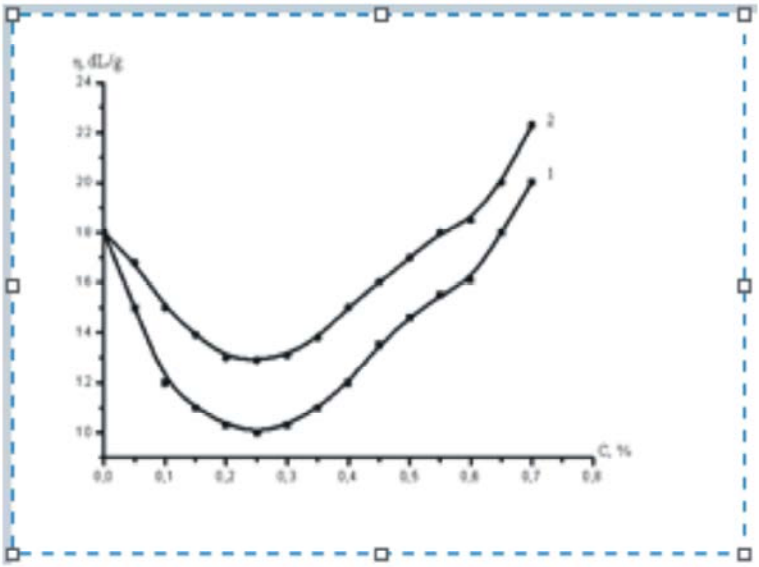

Fig. 6: Effect of sugar substitutes concentration of on relative viscosity of 0.02 % agar solution: 1 – stevioside; 2 – sorbitol

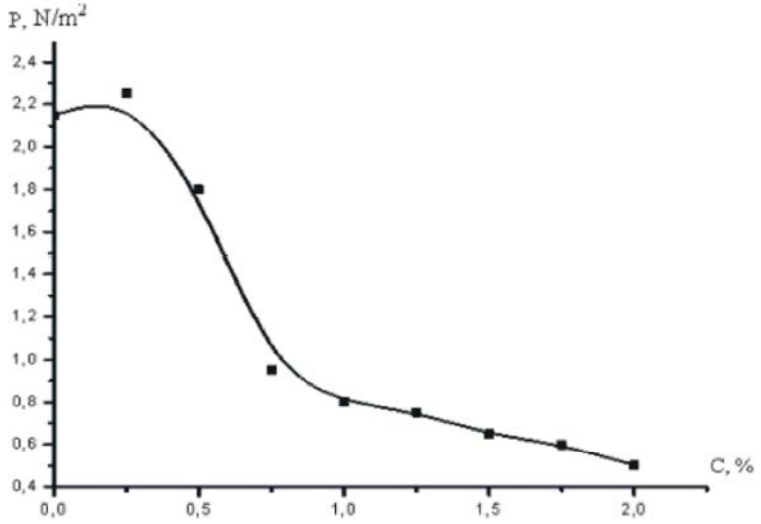

Fig. 7: Effect of citric acid on the strength of agar and Jerusalem artichoke gels. C_{agar} = 1.0 %

Of particular interest is the elucidation of the effect of citric acid on the structuring of food systems based on agar and Jerusalem artichoke, as it is one of the basic components of the confectionery gels. Usually, in food systems, citric acid is used as acidity regulator, however it also has preservative action on the system.

Determination of the strength of the mixture of 1.0% of agar, 25% of Jerusalem artichoke and 0.5% of stevioside in the presence of citric acid (Fig. 7) showed that the addition of citric acid into the mixture leads to a sharp decrease of strength values, starting from 0.25 % concentration. This can be caused by the competition of the citric acid molecules with the components of the system for formation of H-bonds, i.e. it participates in the formation of hydrogen bonds, impoverishing the structuring of polymer phase. On the other hand, the tendency to association and, therefore, to structuring of polymer systems, is closely linked with the quality of the solvent. The quality of water as solvent can be controlled using hydrotropes [19]. These substances destroy the native structure of water, weakening the hydrophobic interactions in it. Therefore, the decrease in the strength of the gels (Fig. 7) under the influence of citric acid can also be justified by of its hydrotrope molecules.

CONCLUSION

Thus, the influence of Jerusalem artichoke Heliantus tuberosus pulp on gelation of agar. It is shown that when injecting Jerusalem artichoke pulp, an increase of the strength of agar gels is observed. Using Weiler-Rehbinder method of determining the strength, IR spectroscopy and viscometry, it was established that the main type of interactions during structuring of the system are the hydrogen bonds between the OH-groups of the polysaccharide and COOH-groups of pectins of Jerusalem artichoke pulp, stabilized by hydrophobic interactions between their non-polar parts.

When structuring the agar in the presence of sugar substitutes, stevioside and sorbitol, increase of their concentration leads to increase in the strength of the gels, which is caused by dehydrating action of sweeteners of food systems. Competitiveness of sugar substitutes and the components of Jerusalem artichoke for the formation of H-bonds and hydrophobic contacts with the macromolecules of agar is shown. In the system of agar and Jerusalem artichoke, introduction of citric acid reduces the strength of the gels due to hydrotropes effect.

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