Influence of sugars on the formation of structural and mechanical characteristics of of agar polysaccharides' gels

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Abstract

Introduction. The current scientific task is to establish differences in structural and mechanical characteristics of agar and k-carrageenan gels with different types of sugars (saccharose, glucose, fructose, lactulose).

Materials and methods. Structural and mechanical characteristics of agar polysaccharides' gels (agar, k-carrageenan) are the instantaneous springy modulus, elastic modulus, springy, elastic and plastic deformation. They were investigated by method of tangential displacement of the plate. There were used model systems of gels on agar and k-carrageenan with saccharose, glucose, fructose and lactulose.

Results and discussion. Gels of agar polysaccharides can withstand different maximum loads depending on the type of sugar. The instantaneous springy modulus had the highest values in gels with saccharose, both on agar and on k-carrageenan, and the values of the modulus of elasticity were higher for gels with monosaccharides. In our opinion, the differences are explained by the difference in the spatial structure and molecular weight of sugars, which imprints on the ability to bind water, that is, hydration ability. Values of total deformation depend on the type of gel: for agar and k-carrageenan gels on different sugars the dependences are different. The greatest value of the total deformation of agar gel has a sample with saccharose – 42.38 c.u. For k-carrageenan gels, the greatest value is the total deformation with monosaccharides. In this case, both agar and k-carrageenan samples with saccharose have higher values of the springy deformation index than the total number of elastic and plastic deformations. However, independently of the polysaccharide, the use of glucose and fructose gives elasticity and plasticity to gel. Adding lactulose to agar polysaccharides' systems leads to a strengthening of the structure of the formed gel, as evidenced by higher values of the force of maximum load for each system.

Conclusions. The individual influence of saccharose, glucose, fructose, lactulose on the structural and mechanical characteristics of gels of agar and k-carrageenan has been established. Disaccharides in general cause greater springy modulus, while monosaccharides cause greater modulus of elasticity of systems and an increase in the total proportion of elastic and plastic deformation.

Introduction

The main raw material for the production of gel-like confectionery products is gel formers of polysaccharide origin, especially agar polysaccharides – agar and k-carrageenan. They form the structure of products in combination with high sugar content [1–3].

In literary sources, the formation of agar polysaccharides' gel is described predominantly with saccharose and the conditions of gel formation and the effect on the formation of the structure of the gel with such sugars as glucose, fructose and lactulose are described insufficiently [4–7]. In this regard, there is a great scientific and practical interest in the study of differences in the formation of structural and mechanical characteristics of agar polysaccharides' gel with different sugars.

Let's consider the conditions of their gel-formation in detail and determine the role of sugars in this mechanism.

Agar or agarose is a complex mixture of sulfated polysaccharides, the main fraction of which is the neutral polysaccharide agarose, which forms a strong gel [8, 9]. Agar gels are formed by the mechanism of cold hardening. Gel-formation is determined exclusively by hydrogen bonds, the presence of which contributes to the formation of single and double helixes. These left-handed spirals are stabilized by water molecules inside the double-helix cavity and by external hydroxyl groups, which makes it possible to aggregate up to 10000 spirals and form microdomains from spherical microgels. The formed gels, as a rule, are solid, fragile, have clearly defined forms, are prone to syneresis and show hysteresis [10].

There is no need for sugar to form an agar gel. Indeed, scientists [11] studied the effect of introduced into the system sugar in a wide range of concentrations. It has been found that an increase in the sugar content leads to a significant increase in the deformation of the gel, reducing the temperature of the gel formation.

Such patterns are associated with the destruction and reorganization of transverse bonds of agarose into a more homogeneous physical grid with the presence of sugars. An increase in the elasticity of the gel was also noted, indicating the formation of a much weaker structural grid and the absence of syneresis.

However, there is evidence [12] that the gel-forming properties of low sulfur agar are enhanced in systems with more than 60% of saccharose. The authors suggest that this synergism is explained by the different inclination of the helix, which depends on the number and distribution of ether sulfate groups.

Carrageenan is a macromolecular linear polysaccharide consisting of repeating disaccharide galactose–3,6–anhydrogalactose fragments (sulfated and non-sulfated), linked by α- (1,3) and (1,4) -β-D-glycosidic alternating rows [13, 14].

Carrageenan gels are formed by the mechanism of ionotropic gel-formation in combination with the mechanism of cold hardening [15]. Gelation involves twisting the polysaccharide chains into helix due to the presence of K^+ or Ca^{2+} ions when cooled. Subsequently, cations contribute not only to the formation of a spiral form of molecules, but also to the coupling of spirals in the zone of connection [16, 17]. Adding additional ions to the system increases the stability of the spiral and promotes its aggregation [18].

Commercially available carrageenans are known as k-kappa, j-yota and λ-lamda, they are obtained artificially and do not exist in isolation in the environment [19]. All of them have very different texture due to differences in the number of sulfate structural groups. Typically, k-carrageenan forms solid brittle gels, in the concentration of gel-former of 0.5–3% [20, 21].

Scientists [22] studied the effect of saccharose and glucose on the dynamic viscosity and springiness of k-carrageenan gels by differential scanning calorimetry. It has been established that Young's dynamic module E 'and the melting point of k-carrageenan gels increased with increasing sugar content, since the amount of heat absorbed during formation of 1 mole of compound zones increased with increasing sugar concentration. It has been suggested that sugars can create zones of connection and stabilize the structure of the bonding zones, but excessive addition of sugars paralyzes the free water that is necessary to form bonding zones.

The thermoreversal gel-formation of water k-carrageenan solution with saccharose (up to 30% by weight) has been investigated using small and large deformation oscillatory rheology [23]. It has been found that saccharose increases the temperature of gel-formation (from 36.8 °C to 52.8 °C) and the melting point (from 51.2 °C to 67.3 °C) to a higher level and enhances the gel net. Studies have shown that, when saccharose is added, tighter and thicker structures of k-carrageenan fibrils are formed. The displacement of the band of infrared spectroscopy of G4S of k-carrageenan and the loss of the vibration band of the free hydroxyl group in saccharose showed the interaction between saccharose and k-carrageenan molecules.

Thus, the information in literary sources, regarding the influence of sugars on the formation of agar polysaccharides' gels is presented rather limited and refers to interactions only with saccharose. Therefore, when developing the technology of products with a gel-like structure and with different types of sugars (glucose, fructose, lactulose), it is important to consider the individuality of each sugar and determine its effect on gel formation and structural and mechanical characteristics of gels. This requires series of experimental studies.

Materials and methods

Materials

To prepare the model gel samples, white crystalline sugar (Agroprodinvest, Ukraine), glucose (Twell Sansino, China), fructose (Vitamin, Ukraine), lactulose (STADA Arzneimittel AG, Germany) agar 1200 (Rokogel, Spain) and k-carraginan purified (Budenheim, Germany) have been used.

Preparation of model systems

In the studies model systems of gels on agar and k-carrageenan have been used: with saccharose (M1, M4), glucose (M2, M5), fructose (M3, M6) (Table 1), and also model systems of gels with lactulose. Lactulose was introduced to replace saccharose (M7, M10), glucose (M8, M11), fructose (M9, M12) in the amount of 10 g of DM / 100 g of gel. Model samples were prepared according to the following scheme: agar was first poured by cold water and left for 20 minutes to swell, then sugar was added, and the mass was boiled to a content of dry matter (DM) of 60%, poured into cuvette with a corrugated plate, cooled and left for gel-formation for 24 hours at t = 18±2°C. For k-carrageenan gels all dry ingredients were mixed, potassium chloride was added additionally in the ratio of 0.1:1 to the polysaccharide and the mass was boiled to 60% of DM, was poured into cuvette with a corrugated plate, was cooled and left for gel-formation for 24 hours at t = 18±2°C.

Table 1

Model samples of gels

Abbreviation	Composition of the components of the system	Prescription ratio of system components, g / per 100 g
M1	agar, saccharose	1.0:60.0
M2	agar, glucose	1.0:60.0
M3	agar, fructose	1.0:60.0
M4	k-carrageenan, saccharose, potassium chloride	0.6:60.0:0.06
M5	k-carrageenan, glucose, potassium chloride	0.6:60.0:0.06
M6	k-carrageenan, fructose, potassium chloride	0.6:60.0:0.06
M7	agar, saccharose, lactulose	1.0:50.0:10.0
M8	agar, glucose, lactulose	1.0:50.0:10.0
M9	agar, fructose, lactulose	1.0: 50.0:10.0
M10	k-carrageenan, saccharose, potassium chloride lactulose	0.6:50.0:0.06:10.0
M11	k-carrageenan, glucose, potassium chloride lactulose	0.6:50.0:0.06:10.0
M12	k-carrageenan, fructose, potassium chloride lactulose	0.6:50.0:0.06:10.0

The structural-mechanical characteristics were determined in the formed gels by the method of tangential displacement of the plate.

Method of tangential displacement of plate

Method of tangential displacement is based on the immersion of the corrugated plate in a newly prepared research system, where after complete structuring of the sample, load is applied from minimum to maximum (with a clear step of variation for each polysaccharide), while fixing graphically the change of deformation in time. A plate is suspended to a quartz or glass spiral spring with a solid thread, connected to laboratory scales (the Vailer-Rebinder method). Applied efforts (load on a cup of scales or lowering the table down in the case of a stretch of the spring) cause displacement of the corrugated plate. Data registration is carried out using an automatic device and a computer program in the form of a curve "deformation – time". On the basis of the obtained curve, values are calculated that characterize the springy-plastic properties of gels. The application of this device allows to obtain a number of curves $\varepsilon = f(\tau)$ quickly (Figure 1), after processing them all other springy-plastic-viscous constants – modulus of instantaneous springyness, modulus of elasticity, general, elastic, springy and plastic deformation are found.

The plate is always set precisely in the middle of the cuvette, in which the investigated system is located. The plate area on both sides should be 10 cm^2. The size of the cuvette is 2×4. For such dimensions, the development of deformation completely passes in the studied systems and the calculation of structural and mechanical constants is simplified (a = 1 cm, S = 10 cm^2). The time for structuring all samples is 24 hours. By short-term sample loads, the weight of the first load is selected with gradually increasing weight. Curve $\varepsilon = f(\tau)$ is recorded during 5 minutes, then the load is removed and after 5 minutes load again, increasing the weight of samples on the cup. Loading and unloading continues until the destruction of the structure – the onset of a conditionally springy rupture, and the stretching of the plate from the sample. The loads are carried out in a way to obtain a minimum of 6–8 deformation curves provided that all the systems under study are measured in a single load range. The resulting curves are interpreted using the «OriginPro» program. The loading ***p (r),*** on the unit area of the plate, is expressed by the voltage of the displacement ***P (Pa)*** and is calculated by the formula:

$$\mathrm{P} = \frac{F}{S}$$

where F = mg is load; m is weight, kg; g is acceleration of the earth's gravity, m/s^2, S is area of the plate, m^2 (S = 10^{-3} m^2).

According to the "deformation-time" curve, springy, elastic and plastic deformations are found for each prototype and the instantaneous springy and elasticity modules are calculated.

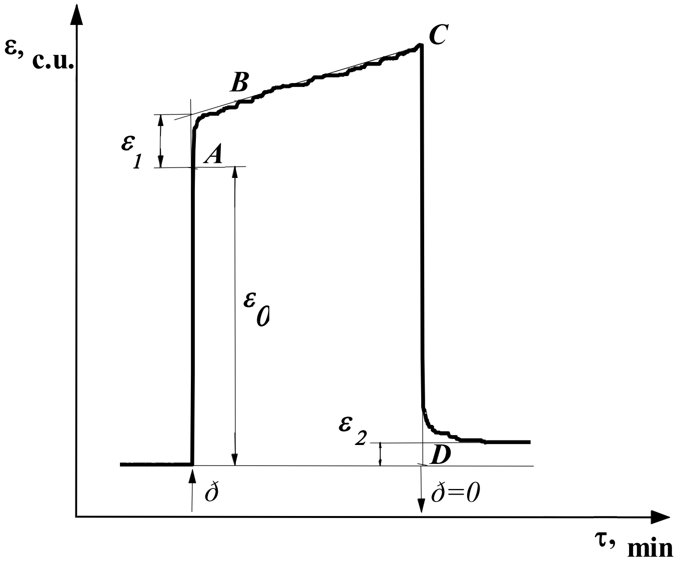

Figure 1. The "deformation-time" curve for an springy-plastic body

The springy deformation **ε_0,** which arises at the moment of applying the load ($\tau = 0$) and disappears after lifting the load at the speed of sound, is characterized by the magnitude of the conditional-instantaneous springy modulus E1, which is calculated by the formula:

$$\mathrm{E1} = \frac{\mathrm{P}}{\varepsilon_0}$$

The elastic deformation ε_1, representing the process of springy aftereffect while maintaining a constant load (p = const) for several minutes, is characterized by the elastic modulus E2, which is calculated by the formula:

$$\mathrm{E2} = \frac{\mathrm{P}}{\varepsilon_1}$$

The elasticity of the gels is due to the stretching of the hydrocolloids' macromolecules shuffled into the balls, which return to the initial state after the removal of the load. The elastic ε_1 and springy ε_0 deformations are mechanically reversible. When lifting the load ($p = 0$) the process goes in the opposite direction and the system returns to the initial state. If the load exceeds the springy limit, a springy gap occurs, or there is a plastic deformation ε_2. In this case, after the instantaneous springy deformation ε_0, along with the decaying springy effect on the AB region, a gradual increase in plastic deformation occurs. The next rectilinear section BC is due to the constant value of plastic deformation (flow). When lifting the load ($p = 0$), the system does not return to the initial state, but differs from the initial value of the residual plastic deformation ε_2. The area CD determines the value of the total deformation of the system in conditional units.

For the correct characterization of the springy-plastic properties of gels, modules are generalized by building the dependences $E_1 = f(P)$, $E_2 = f(P)$, and extrapolating the values of the modules to $P = 0$.

The value of springy, elastic and plastic deformation is presented in percentage terms to general deformation, in order to facilitate their perception.

Results and discussion

The type of the structure-forming agent and the mechanism of its gel formation determines the nature of the structure of the formed gel [24, 25]. And the structural and mechanical properties of gel will depend on the individual effects of sugar used in the system. The results of the determination are presented in the Figure 2 and show that agar polysaccharides' gels can withstand different loads depending on the type of sugar.

Thus, agar gels (sample № 1) with saccharose, glucose, fructose can withstand the same load of 2449.3 Pa, and gels of k-carrageenan (sample № 2) have dependence of the strength on sugar: with saccharose – 1126.3 Pa, with glucose – 920.5 Pa, with fructose – 1028.2 Pa. This suggests that sugars play a less significant role in the mechanism of agar formation in comparison with k-carrageenan [26, 27]. Samples of k-carrageenan and monosaccharides are inferior to samples on saccharose due to the strength of their structure. And fructose can withstand greater load than glucose.

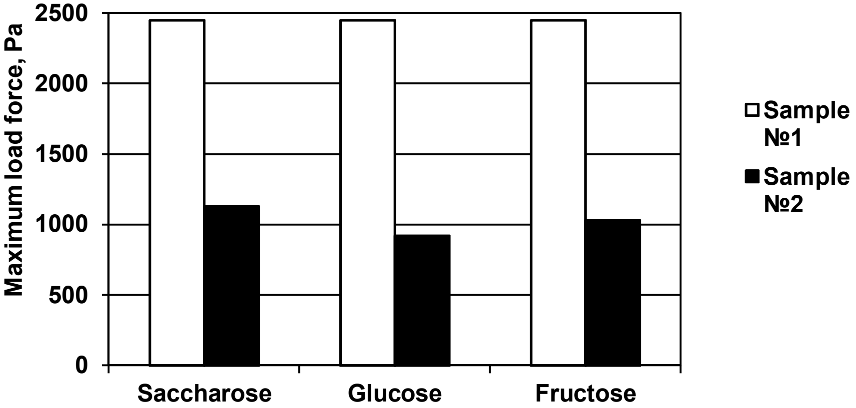

Figure 2. Maximum load force on agar and k-carrageenan gel

In addition, model systems are characterized by various structural and mechanical indicators: springyness, elasticity, plasticity. The instantaneous springy modulus (E1), which characterizes the instantaneous springy deformation that occurs at the moment of loading, and the elastic modulus (E2), which characterizes the springy aftereffect in time, are presented in the Table 2 for the experimental samples.

Table 2

Springy-plastic characteristics of model gel samples

Sample	Module, kPa (P=0)	
	of instantaneous springiness, E1	of elasticity, E2
M1	218.67	438.70
M2	168.78	612.13
M3	117.10	950.45
M4	158.98	125.96
M5	144.53	325.28
M6	99.74	600.00

It has been determined that saccharose gels in the system on agar as well as on k-carrageenan have the largest instantaneous springy module. For example, in model systems on agar with saccharose (M1) the value of E1 is 218.67, kPa, with glucose (M2) – 168.78 (23% less), with fructose (M3) – 117.10 (by 46% less) kPa; in the model systems on k-carrageenan with saccharose (M4), the E1 value is 158.98 kPa, glucose (M5) – 144.53 kPa (10% less), fructose (M6) – 99.74 kPa (37% less)

The values of the modulus of elasticity have an inverse relationship. Thus, saccharose gels in agar polysaccharides' systems have the smallest modulus of elasticity. For example, in model systems on agar with saccharose (M1), the E2 value is 438.7 kPa, with glucose (M2) – 612.13 kPa (more by 39%), with fructose (M3) – 950 kPa (more by 117%); in the model systems on k-carrageenan with saccharose (M4) the value of E2 is 125.96 kPa, with glucose (M5) – 325.28 kPa (more by 158%), with fructose (M6) – 600 kPa (more by 376%)

More specifically, the effect of sugars on the springy-plastic characteristics of agar or k-carrageenan gels is due to the correlation between the types of deformation under the action of the same loading for samples is given in Table 3.

It was found that among samples of agar gels, the greatest value of total deformation has a sample with saccharose (M1) – 42.38 c.u., glucose sample (M2) – 28.85 c.u., with fructose (M3) – 28.87 c.u., which is 32% less.

In our opinion, such patterns confirm the peculiarities of the structure-formation of the polysaccharides themselves. As indicated in the literary review, sugars negatively affect the formation of a three-dimensional grid of agar gel, preventing the formation of hydrogen bonds necessary for cross-linking polysaccharide chains. Saccharose, which has a higher molecular weight, a greater total amount of hydrogen reactive groups, prevents the interconnection of agar macromolecules. In turn, the molecules of monosaccharides with less hydrophilic bonds will have a less negative effect on the interaction of agar molecules and the formation of a gel net, which affects the resulting lower values of total deformation.

Table 3

Degree and character of deformation of model gel samples

Sample	Shear stress which is compared to P, Pa	Deformation			
		general c. u.	springy, %	elastic, %	plastic, %
M1	2449.31	42.38	86.44	8.20	4.06
M2		28.85	77.52	17.12	5.36
M3		28.87	74.14	21.60	4.26
M4	783.31	31.35	69.57	27.90	2.53
M5		37.96	67.83	25.06	7.11
M6		36.95	59.86	33.11	7.03

For k-carrageenan gels, there is an inverse relationship: the total deformation of the sample with saccharose (M4) is the smallest – 31.35 c.u.; with glucose (M5) – 37.96 c.u., which is 21% higher; with fructose (M6) – 36.95 c.u., more by 18%.

In the ionotropic gel-formation mechanism of k-carrageenan, cross-linking of polysaccharide molecules occurs at a higher rate due to the formation of potassium bridges. Therefore, the presence in large concentrations of sugar does not inhibit gel- formation, and directly affects the degree of binding of free water. Keeping a larger number of water molecules in the matrix space of the k-carrageenan gel, saccharose forms a stronger structure than gels with monosaccharides.

It is determined that the greatest value of the total deformation for all experimental samples has the springy fraction. In this case, both agar and k-carrageenan samples with saccharose (M1, M4) have higher values of the springy deformation index than the total amount of elastic and plastic deformations. It is also confirmed organoleptically – gel with saccharose has more brittle and firm consistency than with monosaccharides, which are characterized by greater elasticity and plasticity. We suggested that greater elasticity and plasticity of gels with monosaccharides are associated with a lower degree of water in the system, as in the case of pectin gels [28].

Thus, the obtained results confirm literary data of the influence of sugars on the formation of agar polysaccharides' gel. It has been found that glucose and fructose have less pronounced effect on the mechanism of agar gel-formation in comparison with saccharose, which contributes to its strength, and in k-carrageenan gels, on the contrary, under the influence of monosaccharides introduced into the system, general deformation increases. However, regardless of the polysaccharide, the use of glucose and fructose give the elasticity and plasticity to the gel.

Determination of the influence of lactulose on the structure of gels was investigated by replacing it with 10 g of sugar, saccharose, glucose, fructose. The same amount is the maximum recommended daily intake of lactulose as a prebiotic. The influence of lactulose on the structural and mechanical characteristics of agar polysaccharides' gels is presented in Figure 4.

It was established that the addition of lactulose to systems with agar polysaccharide leads to a strengthening of the structure of the formed gel, as evidenced by higher values of the maximum load strength maintained by each system.

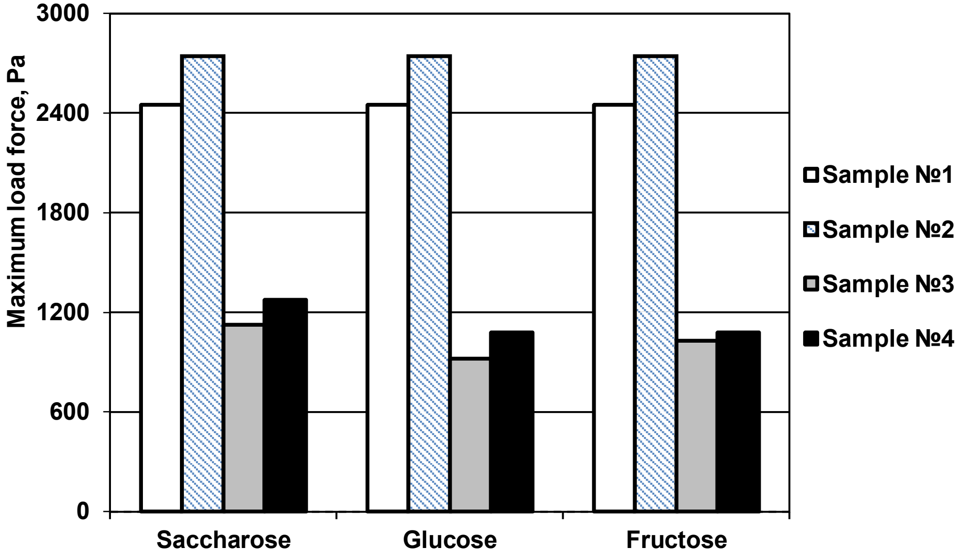

Figure 4. Maximum loading force on agar and k-carrageenan gels without and with addition of lactulose

For example, the loading force of agar gel with saccharose, glucose and fructose (sample № 2) increases by 11% – up to 2714.01 Pa, compared to the basic samples (sample № 1); k-carrageenan gel (sample №4) with saccharose – by 13%, up to 1273.11 Pa, with glucose and fructose – up to 1077.41, 19% and 5%, relative to basic samples of gel (sample № 3). We assume that the addition of sugar, which has a higher molecular weight, will have a greater impact on the viscosity and density of solutions, which leads to the strengthening of the system as a whole. Particularly noteworthy is the strengthening of the structure of gels with monosaccharides, which in our opinion is associated with an increase in the total number of hydration of sugars, and consequently – greater binding of water and structuring of the system.

The confirmation of the above results was also found in the analysis of the nature of deformation of samples of gels, Figures 5–6.

The introduction of lactulose into samples of agar gels leads to an increase in the proportion of springy deformation in the sample with saccharose (M7) by 5.2%, with glucose (M8) and fructose (M9) by 15.4% and 18.0%, respectively. While the proportion of elastic deformation naturally decreases for samples with monosaccharides (M8 and M9) by 72.6% and 63.3%, respectively. It is also organoleptically noted that the consistency of gels with the addition of lactulose becomes more solid and fragile, which confirms the results of increasing the springyness of the system.

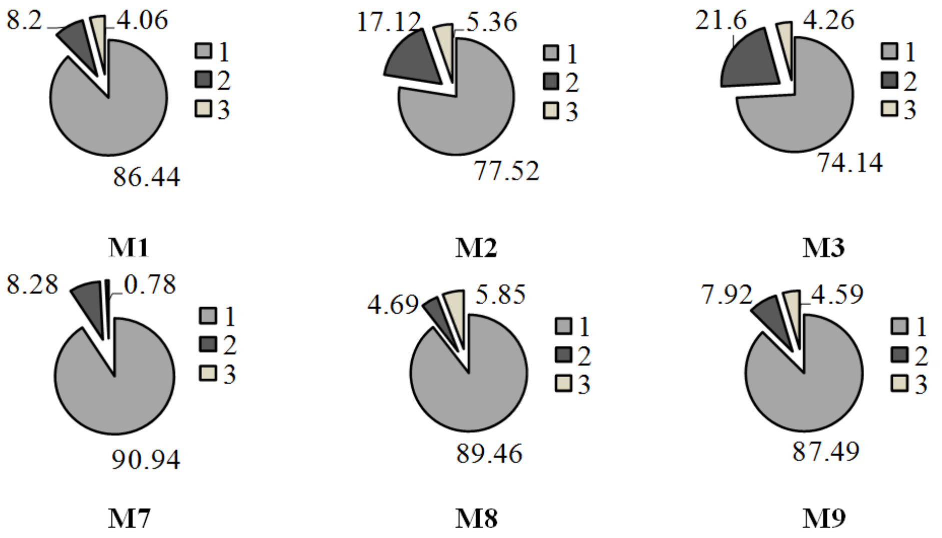

Figure 5. Deformation (1-springy, 2-elastic, 3-plastic) of basic (M1-M3) samples of agar gels and with the addition of lactulose (M7–M9)

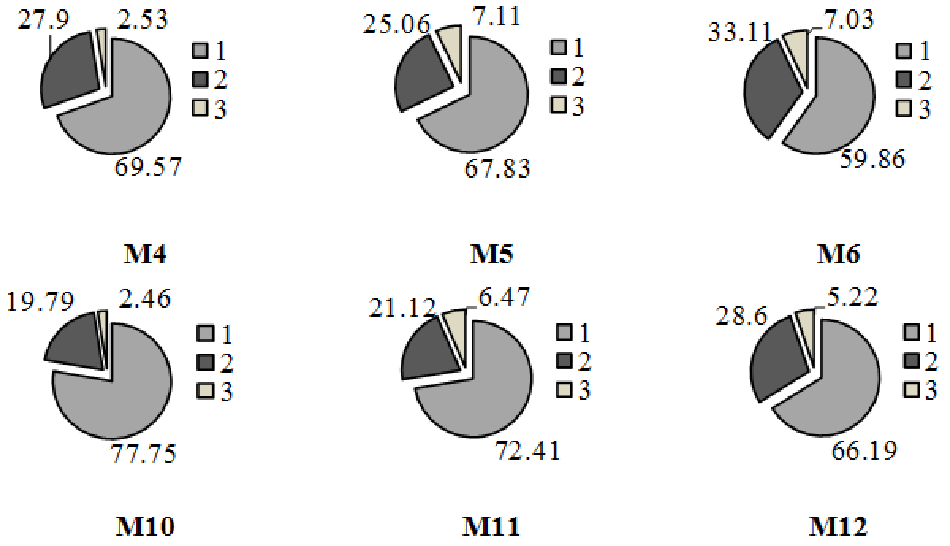

Figure 6. Deformation (1-springy, 2-elastic, 3-plastic) of basic (M4–M6) samples of k-carrageenan gels without and with addition of lactulose (M10-M12)

The addition of lactulose into samples of k-carrageenan gels has a similar effect to agar gels: the proportion of springy deformation increases in the sample with saccharose (M10) by 10.5%, with glucose (M11) and fructose (M12) – by 6.3% and 9.5%, respectively. While the proportion of elastic deformation naturally decreases for samples with saccharose (M10) by 29.0%, samples with monosaccharides (M11 and M12) by 15.7% and 13.6%, respectively.

Conclusion

Based on the obtained results, the following conclusions can be made:

1. It has been established that gels of agar polysaccharides can withstand different maximum loads depending on the type of sugar. Examples of k-carrageenan and monosaccharides are inferior to samples with saccharose, which in our opinion is due to different molecular weight and solubility of sugars. In the model agar gel systems with any experimental sugar the magnitude of the applied load is the same. That is, sugar in the mechanism of agar formation plays a smaller role.
2. It has been determined that the instantaneous springy modulus had the highest values in gels with saccharose, both on agar and on k-carrageenan, and the values of the modulus of elasticity were higher for gels with monosaccharides. In our opinion, the differences are explained by the difference in the spatial structure and molecular weight of sugars, which imprints on the ability to bind water, that is, hydration ability.
3. It has been established that the values of total deformation depend on the type of gel: for agar and k-carrageenan gels on different sugars the dependences are different. The greatest value of the total deformation of agar gel has a sample with saccharose – 42.38 c.u. For k-carrageenan gels, the greatest value is the total deformation with monosaccharides. In this case, both agar and k-carrageenan samples with saccharose have higher values of the springy deformation index than the total number of elastic and plastic deformations. However, independently of the polysaccharide, the use of glucose and fructose gives elasticity and plasticity to gel.
4. Adding lactulose to agar polysaccharides' systems leads to a strengthening of the structure of the formed gel, as evidenced by higher values of the force of maximum load for each system. Particularly noteworthy is the strengthening of the structure of monosaccharides. The obtained results, in our opinion, are related to an increase in the total number of hydration of sugars, and hence to a greater binding of water and structuring of the system.

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