

**РЕОЛОГІЧНІ ВЛАСТИВОСТІ ГЕЛІВ ХАРЧОВИХ  
ПЛІВКОУТВОРЮЮЧИХ НА ОСНОВІ  
УРОНАТНИХ ПОЛІСАХАРИДІВ**

**Н.В. Кондратюк, Є.П. Пивоваров, А.М. Падалка, Є.А. Поливанов**

*Вивчено реологічні властивості гелів харчових плівкоутворюючих на основі композиції пектину низькоетерифікованого амідованого з альгінатом натрію, що містить велику кількість гулуронатних залишків. Гелі харчові плівкоутворюючі мають виражені властивості неньютонівських рідин. Досліджено залежність динамічної в'язкості від часу деформації гелів харчових за сталої швидкості зсуву.*

***Ключові слова:** пектин, альгінат натрію, гелі харчові, реологічні властивості, уронатні полісахариди.*

**РЕОЛОГИЧЕСКИЕ СВОЙСТВА ГЕЛЕЙ ПИЩЕВЫХ  
ПЛЕНКООБРАЗУЮЩИХ НА ОСНОВЕ  
УРОНАТНЫХ ПОЛИСАХАРИДОВ**

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*Изучены реологические свойства гелей пищевых пленкообразующих на основе композиции пектина низкоэтерифицированного амидированного с альгинатом натрия, содержащего повышенное количество гулуронатных остатков. Гели пищевые пленкообразующие обладают выраженными свойствами неньютоновских жидкостей. Исследована зависимость динамической вязкости от времени деформации гелей пищевых при постоянной скорости сдвига.*

***Ключевые слова:** пектин, альгинат натрия, гели пищевые, реологические свойства, уронатные полисахариды.*

**RHEOLOGICAL PROPERTIES OF FOOD FILM-FORMING GELS  
ON THE BASIS OF UROCONATE POLYSACCHARIDES**

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*The effect of the composition of a mixture of uronate polysaccharides on the rheological properties of food film-forming gels was studied. The rheological features of 2% solutions (based on the total solids content) of sodium alginate with a high content of guluronates and low-esterified amidated pectin were investigated. The investigation systems are presented by the viscosity of the plastic matter and*

*possess all the rheological properties of non-Newtonian fluids. In the course of the study we have got to know that the rheological characteristics of such liquids do not depend on the duration of the shear flow and remain constant in time. The dependence of the dynamic viscosity on the time of deformation of food gels at a constant shear rate was studied. From the analysis of the obtained rheological parameters it can be concluded that the structure of the gels is almost completely restored at low shear rates, even in the samples with the highest viscosity. As the shear rate increases, the destruction of the structures begins to predominate over the reduction process, and therefore the viscosity decreases. It is noted that the flow rheograms are non-linear over the whole range of the velocity measurements, which indicates that significant deformation stresses must be applied to destroy the structures. The rheogram shows that taking into consideration both a certain ratio of polysaccharides and the fact that due to the realization of the effect of the electrostatic interaction between the groups having a partially negative charge (-COOH, -OH) and partially positive charge (-COO Na, -CH<sub>3</sub>, -NH<sub>2</sub>), we can observe the effect of gel consolidation, based on the redistribution of the functional groups within the polysaccharide matrix. At the same time the compounds of hydrogen and water molecules are destroyed and they are removed into the outer layers of the gel matrix. It was shown that the composition of sodium alginate and low-esterified amidated pectin with the ratio of 1.6:0.4 respectively, turned out to be the most optimal by the values of the rheological parameters. The rheological parameters of this system are able to ensure the efficient fluidity from the dosing mechanisms, the ability to spread along the flat surface, and the adhesion to solid food surfaces aimed to fulfil a number of technological and production tasks.*

**Keywords:** *pectin, sodium alginate, food gels, rheological properties, uronate polysaccharides.*

**Statement of the problem.** The food film-forming gels based on uronate polysaccharides can be found among the most promising materials, including those used for the production of biodegradable coatings (shells) capable for self-organizing under the standard conditions. To obtain such coatings, sodium alginate and low-esterified pectin compositions have become widely used in recent year [1; 2].

Previously, we studied the chemical composition of sodium alginate and pectin and found out that both of these polysaccharides contain the residues of uronate acids and belong to the class of uronides [3]. Also, considering the ability of both polysaccharides to form the ionotropic gels, where the role of "crosslinking" agents is performed by the ions of bi- or polyvalent metals, in particular calcium [4; 5], the possibility of their combination, followed by the formation of a composite gel, was predicted.

The long-term commercial success of alginate and pectin showed the importance of the consumption of byproducts in the processing of brown seaweed, fruit, vegetables as a source of raw material for the production of gel-forming polysaccharides. Only in 2013, pectin was sold for 850 million US dollars. In addition, the market is expected to grow by this position to

5–6% per year [6]. Moreover, new opportunities for the use of uronate polysaccharides both as individual ingredients and food constituents are being discovered. Therefore, to solve the technological problems of different complexity, the rheological methods for studying the colloidal systems, in particular, the dynamic rheology method, are used.

The rheological method makes it possible to determine the range of ductility and fluidity of the systems under study, to optimize the combination of the concentrations of polysaccharides for the subsequent effective implementation of the technological tasks and requirements for the finished product.

Unfortunately, the available literature data on the rheological properties of the compositions based on high-guluronate sodium alginate and low-esterified amidated pectin are extremely limited. In addition, the analysis of the existing data set does not fully provide an understanding of the features of the structure formation of colloidal systems of these compositions.

In this connection, the search for the new approaches and the optimization of the existing ones, used to study the rheological parameters of the systems based on uronate polysaccharides containing given chemical and phase composition, determining the morphological, structural and physicochemical features of the resulting food gels and coatings based on them, is undoubtedly important.

**Review of the latest research and publications.** The technology used to obtain many biopolymer materials, including self-organizing and biodegradable coatings (shells), involves the ability of the raw material to be changed into liquid (most often in the form of gel), which allows various methods to regulate the structural, mechanical and operational properties of the final products. One of the main trends in the development of the modern materials investigation is the study of the mechanism of the structural formation, as well as the development of the methods implemented to regulate the rheological properties [7].

The use of the macromolecules of pectin and alginate as a polymer stabilizing shell is determined by a number of their unique properties, combining polyfunctionality, nontoxicity, hydrophilicity and their own physiological activity [3; 4; 5], which are prerequisites aimed to create the poly-functional materials in many industries.

As we have studied before [10], the properties of solutions (hydrogels), obtained from the composition of uronate polysaccharides, are a complex system that depends both on the properties of the individual components and on their interaction with each other in the solvent (water). The electrostatic effects that arise during the interaction of functional groups of polymer fibers both with each other and the solvent molecules, are particularly significant.

The prospects for the practical use of compositions based on high-hyaluronic sodium alginate and low-esterified amidated pectin, used as the materials for the creation of food film-forming gels, are determined by the sufficient resources of pectin and alginate-containing materials, which include all plant-based raw materials and brown seaweed.

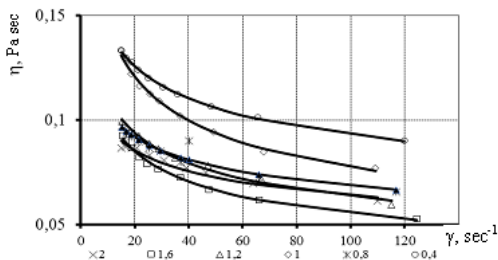
The advantage of the synthesized composites based on uronate polysaccharides is represented by the subsequent possibility of their "crosslinking" fulfilled with the help of calcium ions, When we can trace the manifestation of the synergism of the properties of each carbohydrate component of the polymer matrix on the one hand, and the high technological characteristics, on the other, which include: high strength, sufficient elasticity, neutrality to taste and smell, the rate of transition from the state of the viscous solution to the elastic-plastic body, followed by solidification [8; 9].

**The objective of the article.** The purpose of this study is to investigate the synthesis and analysis of the physical and chemical characteristics of food film-forming gels on the basis of compositions of the uronate polysaccharides.

**Presentation of the research.** The rheological properties of food film-forming gels, based on the alginate sodium and pectin composition containing various ratios of polysaccharides, were investigated with the help of the rotational viscometer VPN-0.2. We have proposed an optimal concentration of the dry substances in a gel solution of 2%, which makes it possible to obtain strong, thermostable films.

When choosing the concentration ratios of polysaccharides, we took into consideration the recommendations of a gradual increase in the amount of one polysaccharide (sodium alginate) in the system of the other (pectin).

The comparison of the rheograms of the investigated samples showed that some rheological parameters differ significantly.



**Fig. 1 Kinetics of the viscosity change in gel samples at a shear rate 100 sec<sup>-1</sup> and pectin concentration: 2,0; 1,6; 1,2; 1,0; 0,8; 0,4%.**

According to the results of the analysis of the rheograms, it was proved that the viscosity of the systems under consideration reflects the formation of a grid of gel based on the uronate polysaccharides, which occurs due to the electrostatic adhesion between the functional groups with partially positive charge (-CH<sub>3</sub>, -NH<sub>2</sub>, -COONa) and partially negative charge (-COOH, -OH), which show their activity in the solvent (water).

In a sample with a pectin concentration of 1,6%, where an "abnormal" decrease in viscosity is fixed, the additional groups (-COONa) appear in the system with a partially positive charge. In this connection, the polysaccharide chains are bound at the points where groups with a partially negative charge are located and the water molecules are squeezed from the volume of the matrix of the polysaccharide gel into its outer layers.

The simultaneous densifying of the polymer fibers and an increase in the number of solvent molecules in the outer layers facilitate the "squeezing" property of the gel between the walls of the rotational viscometer during testing and is reflected by a decrease in the viscosity index at a fixed shear stress. This is the way to form the gel layer in the form of a chain of the interwoven polysaccharide fibers of alginate and pectin concentrated as close as possible to each other by the electrostatic adhesion.

The subsequent increase in viscosity from 0,063 to 0,079 Pa.S, as a result of the application of a component with a denser consistency (1% sodium alginate solution) and, correspondingly, a new portion of the positively charged particles able for redistribution, indicates the further binding of the functional groups by the electrostatic forces adhesion in the system of polysaccharides with the implementation of a solvent. An even larger increase in the number of the positively charged particles (a sample with a sodium alginate content of 1,2%) followed by the implementation of the "densifying" and "squeezing" mechanisms described above again leads to a decrease in viscosity (from 0,079 to 0,070 Pa. S) and allows us to speak about the formation of the new chains of the intertwined fibers of uronate polysaccharides.

The further changes in the ratio of the concentrations of polysaccharides towards the increasing of the content of sodium alginate (up to 1,6%) are not accompanied by a decrease in viscosity, but, on the contrary, by a gradual increase in viscosity, which indicates the completion of the migration processes of the solvent molecules and the ordering of the matrix gel system as a result of the increasing of the compensatory charge in the functional groups.

**Conclusions.** The rheological properties of gels of food film-forming on the basis of uronides (high-guluronate sodium alginate and low-esterified amidated pectin) containing a total polysaccharide concentration of 2% have been analyzed. The concentration ratios of "pectin to alginate" were represented by the following values: 2:0; 1,6:0,4; 1,2:0,8; 1,0:1,0; 0,8:1,2; 0,4:1,6; 0:2. The established nature of the fluidity in the samples indicates the complexity of the interactions in the system under investigation. Thus, in a sample where the alginate to pectin ratio was of 1,6:0,4, 1,0:1,0, the jumps of viscosity in the place of dilution were observed, respectively. The unstable fluidity regime is observed at high shear rates. The decrease in viscosity is explained by the orientation of the dispersed phase along the fluidity direction. Since the process of gel formation takes place according to the terms of the process of structure formation for these dispersed systems, the question of the orientation of the dispersed phase was analyzed from the position of the electrostatic interaction of the functional groups of the polymer fibers of high-guluronate sodium alginate and low-esterified amidated pectin both with each other and with the solvent molecules.

From the analysis of the obtained rheological parameters it can be concluded that at low shear rates the structure of the gels is almost completely restored, even in the samples with the highest viscosity. As the shear rate increases, the destruction of the structures begins to predominate over the reduction process, and therefore the viscosity decreases. It is noted that fluidity rheological diagrams over the whole range of velocity measurements are non-linear, which indicates that significant deformation stresses must be applied to destroy the structures.

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