INVESTIGATION OF THE FILMS BASED ON THE URONATE POLYSACCHARIDES BY THE METHOD OF DIFFERENTIAL SCANNING CALORIMETRY

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Abstract. In this paper, the problem of studying the films properties on the basis of uronate polysaccharides (sodium algininate and pectin low-esterified amidated), created on the principle of ionotropic gelation with the participation of calcium ions, has been considered. The purpose of the study is to determine the patterns of films formation based on the composition of the uronate polysaccharides, to determine their properties when heated and conditions of destruction or combustion. The thermophysical properties of the films in the temperature range 20–500°C were controlled by the method of differential scanning calorimetry in the dynamic mode. The temperature at which the loss of external and internal moisture is occurring have been determined. The temperatures when films are subjected to destruction have been founded. Thus, the mass loss of samples was noted in the following temperature ranges: 52–100°C and 40–100°C; the maximum moisture loss was noted at 83 and 85°C for specimens with a total concentration of uronate polysaccharides 2% and 3% respectively. Maximum external moisture losses were 6% and 9%; intra-linked moisture – 28.5 and 29% respectively. Complete disintegration of polymers occurs after 300 and 310°C for specimens with a total concentration of uronate polysaccharides 2% and 3% respectively. The investigation of the destruction temperatures of the above systems allows us to predict the principle of heat treatment of semi-finished products contained in films, created on the basis of the reaction of ionotropic gelation of polysaccharides and calcium ions.

Key words: food films, uronate polysaccharides, ionotropic gelation, differential scanning calorimetry.

ДОСЛІДЖЕННЯ ПЛІВОК НА ОСНОВІ УРОНАТНИХ ПОЛІСАХАРИДІВ МЕТОДОМ ДИФЕРЕНЦІАЛНОЇ СКАНЮЧОЮ КАЛОРИМЕТРІЇ

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Анотація. У даній статті розглядається питання вивчення властивостей плівок на основі уронатних полісахаридів (алгинат натрію і пектин низькоетерифікованого амідованого), створених на основі іонотропного гелеутворення за участю іонів кальцію. Мета дослідження – встановити закономірності формування плівок на основі композиції уронатних полісахаридів, визначити їх властивості при нагріванні та умови деструкції або загоєння. Методом диференційної скануючої калориметрії у динамічному режимі було здійснено контроль теплофізичних властивостей плівок у діапазоні температур 20–500°C. Встановлено температури фазових перетворень. Визначено, за яких температур відбувається втрача зовнішньої та внутрішньої вологи. Зазначено температури, за яких плівки підлягають деструкції. Так, втрача маси зразків була відмічена у наступних діапазонах температур: 52–100°C та 40–100°C; максимальна втрача вологої припадає на 83 і 85°C для зразків із загальною концентрацією уронатних полісахаридів 2% та 3% відповідно. Максимальна втрача зовнішньої вологи становили 6% та 9%; внутрішньої – 28,5 та 29% відповідно. Повний розпад полімерних зразків настає після 300 і 310°C для зразків із загальною концентрацією уронатних полісахаридів 2% та 3% відповідно. Дослідження температур деструкції окреслює досліджуючи системи можливість прогнозувати принцип теплової обробки напівфабрикатів, що знаходяться у плівках, створених на основі реакції іонотропного гелеутворення між полісахаридним гідрогелем, сформованої на основі взаємодії гідроколоїдних систем альгінату натрію (1 та 1,5%-ві розчини) та пектину низькоетерифікованого амідованого (1 і 1,5%-ві розчини) загальною вмістом уронатних полісахаридів 2 та 3% відповідно, з іонами кальцію, які містяться у 0,5 % розчині СаСl₂.

Ключові слова: харчові плівки, уронатні полісахариди, іонотропне гелеутворення, диференційна скануюча калориметрія.

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Introduction. Formulation of the problem

The high level of danger from the excessive amount of polymer waste influence is an actual problem at the present time. There are about 300 million tons of plastic products are produced annually in the world, almost 60 million tons of which are food packaging. Therefore, biodegradable packaging creation is a promising direction in solving the ecology problems [1,2].

There are quite popular trends of creating different types packaging materials. These technologies are based on physical and chemical properties and chemical potential of proteins and peptide complexes, polysaccharides, polyols, polylactic acid, etc. Different “crosslinking” agents are used to strengthen the materials [3,4]. Salts of bio non-organic elements, in particular of calcium, play a special role.

Composites, based on sodium alginate (NaAlg) and pectin low-esterified amidated (LEAPectin), are increasingly becoming the basis of gel systems modern study. Scientists from different countries see the strategy of their use as healing wound healing materials together with the polysaccharide gel included in the matrix of antiseptic substances (zinc and polyglycerol) [5], antioxidant (ascorbic acid) [6], etc.

Gels based on sodium alginate and low-esterified amidated pectin has a series of technological properties. They are in great demand of various industries in the food industry as stabilizers and thickeners. The rheological models of such systems were studied in the scientific schools of Norway and Poland [7,8]. Nevertheless, there is no information in the literature about xerogels as a product of phase transformations, which are presented as food envelopes on the surface of the product after application and drying.

Analysis of recent research and publications

Gels are a disperse systems with liquid dispersion medium in which a particles of the dispersed phase (gel formers) form a spatial structural grid. This is the basis of the concept an envelope forming food gels based on uronate polysaccharides. Gels are able to keep shape, but at the same time they exhibit elastic and plastic properties.

These systems are the most justifiable in technological terms because these polysaccharides can high reactivity to the formation of spatial structures due to the implementation of the principle of ionotropic gel formation.

After analyzing the chemical composition of these polysaccharides it was concluded that they belong to the same class called “polymuronides”. Due to the same nature of origin, the resulting food compositions are polymeric gels swollen in a solvent (water) under standard conditions. Chains herewith interact with inter-chain covalent bonds in a single spatial grid, while holding multiple amounts of moisture.

The mechanism of ionotropic gel formation in the system of sodium alginate [9] and low-esterified amidated pectin with calcium [10] was thoroughly studied. Binding occurs between the four carboxyl groups, predominantly of the guluronate blocks with the participation of sodium alginate. Instead, in the structure of low-esterified pectin formation of a chelating complex with calcium occur between the four residues of galacturonic acid containing deprotonated carboxyl groups.

The above-mentioned information was the starting point for the idea of creating “cross-copolymers” of the irregular structure due to the identity of the chemical structure the indicated polysaccharides. The role of “cross-agents” reserved for calcium ions due to its high reactivity to the creation of spatial gel nets.

The mechanism of the “cross-copolymers” formation is the interaction with the metal ion of two linear chains: low-esterified amidated pectin and high content of G-blocks sodium alginate (Fig. 1).

Fig. 1. Quantum-chemical model of complex of guluronate (2Gul) and galacturonate (2Gal) dimers, cross-linked with calcium ion (Ca$^{2+}$)

Thereby, study of «cross-copolymerization» process in the «alginate-pectin» system at the realization of ionotropic gel formation mechanism is one of latest approach in the field of food engineering in the issues of creating a biopolymer food coating technology (envelopes, packs, utensils, etc.). They decompose in conditions of pH increasing to the level of 8.0 and serve as a good substrate for microorganisms of the intestine in case of getting into the human body or warm-blooded animals.
A phase transition are possible at the same time. Usually, they caused by increasing of attraction between the links of the grid. This can lead to the displacement of water from the gel into the outer solution. The sharp attraction of the chains that is a sharp decrease in the volume of the gel with slight changes in the external conditions is called collapse. That is why hydrogels based on compositions of the uronates called «smart or intelligent materials» [11,12], namely materials which able to react instantly to minor changes in the environment according to a pre-programmed plan.

Nowadays the conformational transitions [10], phase transformations [13] and technological properties [14] in food gels based on uronate polysaccharides as sodium alginate and low-esterified amidated pectin are studied actively. Such resulting of ionotropic gel formation structures can be evaluated as promising material to food envelopes (xerogels) getting, operating in the range of pH from 1.0 to 7.5. There are strong, elastic and form-resistant structures in this range of pH [15].

Consequently, search and optimization of new approaches to creating compatible compositions based on uronate polysaccharides which are the envelope forming food gels with given chemical and physical composition, which determine the morphological, structural, texture and physiological features of food coatings, the thermophysical properties of which are described in this article are very relevant.

The thin envelopes investigation based on uronate polysaccharides is interesting both from a practical and a scientific point of view. It gives information about substance properties changes during the transition from the three-dimensional spatial dimension of the polymer chains location, combined with calcium, which is formed in a hydrogel, to two-dimensional, which describes thin envelopes. The study of phase transitions in systems with reduced dimensionality, which forms the notion of the finished product quality, is particularly interesting. However, data on the thermal properties of such systems are extremely limited, but necessary to determine the range of practical usage of new material, which has unique characteristics that can be used in the production of various types of food products.

Method of differential scanning calorimetry (DSC) is one of the effective to study the thermal properties of the envelopes forming food gels based on uronate polysaccharides. It consists in determining the basic thermophysical characteristics of the investigated objects with the help of a calorimeter.

The purpose of this research is the investigation of the external and internal moisture content in the composition of food films on the basis of uronate polysaccharides compositions and cross-linking with calcium ions and the determination of the range of temperatures at which the investigated objects are resistant to thermal processes.

Tasks of the work:
1. To analyze conditions and factors for the formation of hydrogels, based on uronate polysaccharides, cross-linked with the calcium and their phase transition to the state of xerogels.
2. To identify the types of moisture present in food envelopes, based on uronate polysaccharides, to study the order of hydrogen bonds and the range of food envelopes stability during heating using the method of differential scanning calorimetry.

**Research Materials and Methods**

A sodium alginate (NaAlg (Algogel 3021, FD-120), «Danisco», Denmark) with the high content of gulurionate residues (up to 70%) and low-esterified amidated pectin (NEC-J-A1, esterification and amidation degree are up to 30% and up to 25% respectively, Poland). A solution of calcium chloride dehydrated with a mass concentration of salt 0.5% was used to make of envelopes.

**Films formation.** Preparation of samples took place in two stages. Hydrogel was formed at the first stage. Weighed portion of an uronate polysaccharides mixture was filled with water by temperature 

\((t=20±2°C)\) during periodic stirring and maintained under standard conditions without restriction of air access for 4 hours. At the second stage structured gel with a layer of 1 mm applied to the surface of food semi-finished products and a 0.5% solution of calcium chloride was immediately aerosol sprayed at a rate of 0.25 ml per 4 cm² area of the product. The samples were ripened. The ionotropic gelation between calcium ions and the carboxylic residues of uronic acids, which form the basis of the uronate polysaccharides, was obtained at the same time. Binding with calcium ions of polysaccharide chains caused the destruction of hydrogen bonds around hydrophilic groups of uronates. Likewise in the phase of hydrogel together with the process of structuring carried out mass transfer of moisture. In this case, the hydrogel phase was gradually converted into xerogel (films). The process of phase change proceeded without limiting air access. The time of phase transformations was 48 hours.

The resulting gel systems are a mixture of "LEA pectin: NaAlg: Ca 2+" in a ratio of 1:1:0.5 (sample 1) and 1.5:1:0.5 (sample 2). According to the results of previous rheological investigations [13] it was found that this ratio is optimal for ensuring the high moisture content of hydrogels and the elasticity and durability of xerogels constructed on their basis.

The thermophysical properties were determined by an effective method of differential scanning calorimetry (DSC) in dynamic mode. Thermograms DSC were obtained in the temperature range 25–500°C at a constant heating rate 5°C/min by calorimeter Derivatograph Q1500-D. The samples were heated to a maximum temperature of 500°C to determine the conditions for their complete decomposition (burning). The sample weighing 50 mg was placed in a ceramic crucible. The temperature determination accuracy was ±1°C, thermal effect was ±3%.
An automatic electrical compensation during the thermal energy changes in the samples was predicted according to the principle of DSC. As a result, the temperature was maintained with the help of a regulator at one and the same level in the phase transformations of the system. Visualization of the process was recreated in MS Excel. Exo-and endothermic peaks were recorded in units of energy. It can be possible from the curves the mass loss during the heating. The peak acreage described the warmth of the reaction. Investigated samples were in the isothermal conditions relative to inert material. The amount of heat needed to maintain isothermal conditions was recorded as a function of time.

**Results of the research and their discussion**

There is a little information about conditions of formation identified gel-like systems especially their phase transformations from hydrogels to xerogels nowadays. Particularly there are no information about the applied aspect of such systems in food engineering. Consequently, study theoretical aspects of these interactions helps in new technologies developing and their implementation into food products and culinary semi-finished products making.

Envelopes have a target functional characteristics included the shelf life of finished products increasing with the saving of high organoleptic parameters. The type of polysaccharides modification and their general content are very important for study of envelopes properties during the heating.

Investigated samples differed of their texture. Envelopes of sample 1 (Fig. 2) were more transparent and elastic but less strong than the envelopes of sample 2.

It must be noted, that in all investigated samples the endothermic melting peak was observed. It indicates about the presence of a phase transition. The temperature in which the investigated objects begin to lose weight was in the range of 52–100°C and 40–100°C for the samples 1 and 2 respectively. The losses of externally bound moisture were determined during the stay of samples in specified range of temperatures. Thus, for the sample 1 they were 6%, for the sample 2–9% of their total mass. Such data show that systems which consists of more polymeric polysaccharide fibers and hold up more amount of external moisture. Thereby, we can to predict that the amount of internally bound moisture will also be different.

The ultimate temperature of the mass transfer of external bound moisture was 134°C for the sample 1 and 145°C for the sample 2. Considering the indicator of the amount of internally bound moisture lost and temperature difference calculations (Δт₁, for the sample 1 it equals 82°C and for the sample 2 Δт₂ equals 105°C), we can conclude that moisture in samples is not lost at the same speed but at the same temperature, because maximum loss accounts for 83 and 85°C respectively.

Research of the envelopes samples behavior for higher heating and the process of internally bonded moisture loss were the next stage of the derivatogram description (Fig. 3).

![Fig. 2. Thermogram of DSC for the thin films based on system «NEA pectin:NaAlg:Ca²⁺» at the ratio of input substances 1:1:0.5 (1 – temperature (T, °C); 2 – DTG)](image)

Initial temperature of the second stage of moisture mass transfer was in range 175–293°C and 159–308°C for the samples 1 and 2 respectively. During the heating of samples in the specified range of temperatures an internally bonded moisture loss for the sample 1 was 28.5%, sample 2–29% from the mass which samples had at the end of the first stage of thermogravimetry. Obtained data lead us to the conclusion that polymer structures of polysaccharides hold the same number of internally bonded moisture.

![Fig. 3. Thermogram of DSC for the thin films based on system «NEA pectin:NaAlg:Ca²⁺» at the ratio of input substances 1.5:1.5:0.5 (1 – temperature (T, °C); 2 – DTG)](image)

Temperature differences at the second stage of the scan for all samples have showed more active moisture loss in samples with a lower concentration of polysaccharides because these systems have a less points of moisture maintenance. Herewith, the maximum moisture loss is accounted for 238 and 244°C respectively.

These results indicate that number of hydrophilic groups does not increase during alginate-pectin cross-linked with the calcium ions “cross-copolymer” formation in the case of an increased number of polymer
chains per unit volume. Conversely, the “contraction” chains effect is realized at the same time. Moreover, reduction of the inter-molecular distance between the chains makes it impossible to include molecules into the polymer gel matrix.

Herewith, taking into account the constancy of volume, the emergence of polysaccharide groups and polymer fibers "contraction" allows free molecules of water, which could not get into the matrix of a polymer gel, to realize its chemical potential for the formation of intermolecular bonds in the outer layers of the gel net and interact with molecules of polysaccharides in hydrophilic binding centers that go outside. This explains the same amount of internally bonded moisture and differences in the values of external moisture in the investigated samples.

Temperature difference in the second stage of the scan for the first sample (ΔT1) was 118°C and for the second sample (ΔT2) – 149°C. It was an important fact in the research. According to the above-described principle of accumulation and maintenance of moisture in the envelopes, we can testify to the more active loss of moisture in samples with a lower concentration of polysaccharides. This is connected with the smaller number of points the moisture content in these systems. There is a water molecules release “blocking” effect from the polysaccharide matrix in a sample with a higher concentration of dry matters due to the closer position of the polymer chains so the time of moisture loss is longer. At the same time, the maximum moisture loss is 238 and 244 °C respectively for samples 1 and 2. The total moisture loss for the investigated objects was 34.5% for a sample 1 and 38% for a sample 2.

Therefore, the dynamic of samples mass loss at temperatures much higher than the temperatures of breakdown the intermolecular bonds with water in the polymer matrix of envelopes indicates about destruction of polymers. Namely, destruction of connections which hold -CH3 and -NH2 groups in pectin begins after removing of moisture. A figures show that after 300 and 310°C the mass of samples remains unchanged. This indicates about a complete destruction of polymers.

As it became known, these systems in the presence of multiple quantities of water are hydrogels polysaccharide fibers of which are cross-linked with the calcium ions. The samples were formed by ionotropic gelation with participation of high guluronate sodium alginate and low esterified amidated pectin. Hydrogels are transformed into xerogels (envelopes) during 24 hours for standard but aseptic conditions without limiting air access. These envelopes are promising in the packaging materials creating and food shells.

The strategy of use pectin and alginate macromolecule as a polymer shell was developed according to the results of quantum-chemical research. Therefore formed models are determined by unique properties, in particular: multifunctionality, non-toxicity, water solubility and own physiological activity. This is a prerequisite for the creation of multifunctional materials in many industries.

The synthesized composites based on uronate polysaccharides cross-linked with the calcium ions advantages are properties synergy of each carbohydrate component of the polymer matrix and high technological characteristics, particularly high strength, sufficient elasticity, transparency, neutrality to taste and smell, fast transition from the state of the viscous-fluid solution to the elastic-plastic body with further strengthening.

**Conclusion**

According to the results of the thermograms analysis, the endothermic melting peak was observed in all investigated samples. It indicates about the presence of a phase transition.

The mass loss of samples was noted in the following temperature ranges 52–100°C and 40–100°C, the maximum loss of moisture accounted for 83 and 85°C for the samples with a general concentration of uronate polysaccharides 2 and 3% respectively.

Maximum loss of external moisture in weighed portion for sample 1 and sample 2 was 6% and 9% respectively, internally bonded moisture loss was 28.5 and 29.0%. These results are shown that systems with large polymeric polysaccharide fibers hold a significant amount of external moisture whilst internally bounded moisture in the samples contains the same amount.

The total moisture loss for the research objects was: sample 1– 34.5% and sample 2–38%. Therefore, the dynamics of mass loss the samples at temperatures much higher than the temperature of the breakdown of intermolecular bonds with water in the polymer matrix of envelopes, indicates the destruction of polymers. Namely, destruction of connections which hold the groups -CH3 and -NH2 in the pectin begins after moisture removing. The total polymers’ destruction comes after 300 and 310°C respectively.

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