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THEORETICAL ASPECTS OF STUDY OF POLYMERIZATION PROCESSES TAKING PLACE DURING FORMING POLYSACCHARIDE HYDROGELS WITH AMINO ACIDS

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ABSTRACT In the article the method of synthesis and analysis of physical and chemical properties of film-forming edible gels basing on compositions of uronic polysaccharides cross-linked with calcium nanoparticles. The prospects for the practical use of synthesized compositions on the basis of high-guluronate sodium alginate and low-ester amidated pectin as materials for provision of film-forming edible gels is determined. The interphase boundary in the composite hydrogel is analyzed, which is a transition layer in which the properties change gradually (transition from the properties of phase 1 to the properties of phase 2), while the second phase, with consideration of interphase interactions, is responsible for morphology of film-forming edible gels. The nature of the interactions between the components that is determined to covalent bonds in block- and graft copolymers, forming interpolymer complexes at the expense of appearances of hydrogen bonds, donor/acceptor, ionic and hydrophobic interactions of functional groups, as well as due to engagements of macromolecular chains in interpenetrating and semi-interpenetrating polymer networks. There were studied functions of low-molecular weight polyuronate fractions in binding calcium and calcium-induced gelling of normal low methoxyl pectin (LMP) - the fractions of pectin with two different degrees of esterification (DE), as well as of alginate with two different mannuronate/ guluronate (M/G). It was established that solution on the basis of P:A (pectin/alginate) compositions have properties of non-Newtonian liquids, which viscosity depends on shear stress. It was found that content of non-film-forming additives shall be within molecular ratios with consideration of binding points. The water solubility of two-ingredient films and their moisture permeability were determined, and it was shown that the solubility increases in proportion with growth of content of cross-linking agents while growth of moisture permeability is just inconsiderable. The results of the work became the scientific basis for the development of technology of food coatings that self-organize and biodegrade under standard conditions.

Keywords: film-forming edible gels; uronic polysaccharides; sodium alginate; low-ester amidated pectin; calcium ions; synthesized composites.

ТЕОРЕТИЧЕСКИЕ АСПЕКТЫ ИЗУЧЕНИЯ ПОЛИМЕРИЗАЦИОННЫХ ПРОЦЕССОВ ПРИ ФОРМИРОВАНИИ ПОЛИСАХАРИДНЫХ ГИДРОГЕЛЕЙ С АМИНОКИСЛОТАМИ

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АННОТАЦИЯ В статье рассмотрено метод синтеза и анализа физико-химических характеристик гелей пищевых пленкообразующих на основе композиций уроновых полисахаридов, сшитых наночастицами кальция. Определена необходимость создания гидрогелей пищевых пленкообразующих. Исследованы функции низкомолекулярных полиуронатных фракций в связывании кальция и индуцированного кальцием гелеобразования нормального низкометокси-пектина. Результаты работы стали научным основанием для разработки технологии пищевых покрытий, что самоорганизуются и биodeградируют при стандартных условиях.

Ключевые слова: гели пищевые пленкообразующие; уроновые полисахариды; альгинат натрия; низкоэтерифицированный пектин; ионы кальция; синтезированные композиты.

Introduction

The film-forming edible gels on the basis of uronic polysaccharides (sodium alginate and low-ester amidated pectin) comprise a promising generation of materials, in particular, coatings for different industries, including food industry and catering business [1].

The most promising is use of such materials in creation organic foods and edible envelopes for many groups of goods, in particular for delivery of finished

products to their destination with possibility of prevention of moisture release from semi-finished products and further mixing flavoring substances. Due to use of the film-forming edible gels, an opportunity of joint transportation of different culinary semi-finished products appears with saving quantity of packaging materials.

This explains an urgent necessity of search for new and optimization of existing approaches to synthesis of compatible materials on the basis of uronic polysaccharides with given chemical and phase

composition, which determine morphological, structural, physical, physiological and toxicological properties of obtained edible coatings [2].

Also an important factor is the type of polysaccharide modification, which determines the possibility of forming the gel spatial network by reaction of ionotropic gelling with metal ions (in particular, calcium ions), with subsequent forming the protective envelope having certain functional characteristics, including increase of shelf life with retention of high sensory parameters [3-5].

Purpose

The purpose of this work is synthesis and analysis of physical and chemical properties of film-forming edible gels basing on compositions of uronic polysaccharides cross-linked with calcium nanoparticles.

Use of pectin and alginate macromolecules as polymeric stabilizing envelope is determined by a number of their unique properties combining polyfunctionality, non-toxicity, water solubility and own physiological activity, which comprises precondition for creation of multifunctional materials in many branches of industry [6].

A great potential of practical use of compositions on the basis of high-gulonate sodium alginate and low-ester amidated pectin as materials for provision of film-forming edible gels is determined by sufficient available resources of pectin- and alginate-containing materials, which are contained in all vegetable raw materials and brown sea algae.

The advantage of the synthesized composites on the basis of uronic polysaccharides cross-linked by calcium ions consists, on the one hand, in synergism of properties of each carbohydrate component of polymeric matrix, and, on the other hand, in their high technological characteristics, in particular: high strength, sufficient elasticity, transparency, neutrality in relation to taste and odor, high speed of transition from viscous-flow condition to elasto-plastic body with subsequent solidifying [7].

Basic material

The films were formed from solution by pouring onto glass surface with subsequent its distribution over the surface with the help of a special attachment – “scraper” having a clearance making it possible to distribute the solution evenly over the glass surface for achievement of uniformed thickness of formed film. Prior to application of solution, the glass substrate was specially prepared by careful washing and drying. The ready solution was applied to the surface in the form of a thin strip, and then the film was formed with the use of the scraper with a clearance of 1 mm.

During forming the film, the temperature was fixed directly before pouring the solution onto substrate. In

some cases, the substrate (glass) was also previously heated.

The freshly formed film was immediately placed in drying box where it was held at strictly defined temperature and time (τ of drying). The forming and drying parameters of all films obtained during this work was chosen with consideration of literature data on gelling temperature of chosen polymer solutions for provision of homogeneity of the forming solutions, as well as thickness of obtained film (the lesser the film thickness, the lesser time it requires for drying). After drying, the films were taken out from the drying box, cooled down to room temperature and removed from the substrate.

For studying influence of forming temperature on mechanical properties of the films obtained by the above methods, there were prepared the solutions with P/A (pectin/alginate) ratios = 100:0; 90:10; 80:20 and 70:30. All solutions contained 2 g of polymers and 100 g of solution. The prepared solutions were removed from thermostat and gradually cooled down to required forming temperature (from 70°C to 30°C). On each of previously prepared glass substrates, from each solution, as it was cooled, five films were formed with the use of scraper having clearance of 1 mm, at forming temperature 70, 60, 50, 40 and 30°C. Each film was placed in drying box just after forming and was dried at 60°C for 30 minutes.

Discussion of the results

Lately, use of edible gels became more desired. They, in addition to hydrophilic properties, also have other target characteristics, such as gas permeability peculiar for hydrophobic materials (polysiloxanes and fluoropolymers), high mechanical strength of material in hydrated condition, compatibility with biological tissues, optical transparency, electrical conductivity, etc. Combination in one material of the said properties makes it possible to create unique products, for example, soft contact lenses with high oxygen permeability, carriers of water insoluble medicines, adsorbents capable of absorption of both hydrophilic and hydrophobic substances, new membrane materials and other products. The said objectives may be achieved due to obtaining principally new materials – composite hydrogels containing at least two ingredients, each of which fulfils certain functions.

However, creation and study of film-forming edible hydrogels became the most prospective line in catering and service industry. It is evident that the characteristics of composite hydrogel are not only based to physical and chemical properties of individual ingredients but also on the material structure. With consideration of practically unlimited thermodynamic compatibility of uronic-nature polymers between each other, between ions of some metals (calcium, magnesium, iron, copper, chromium), as well as possibility of provision of polymeric matrices cross-linked with amino acids (glycine, threonine, cysteine), even with inclusion of

fatty acids (oleic, linoleic, linolenic) as branching agents, it became possible to form hydrogels of different composition, beginning from dense polysaccharide gel to forming structures of "matrix/nanosized inclusions" type or appearance of structures, in which both polymeric phases are continuous [8].

In case of connection in one composite hydrogel of two hydrophilic polymers, the morphology of the material is not always evident. Taking into account an obligatory presence in the hydrogel of one more ingredient (water), we can suppose that in some cases, this ingredient may serve as a solvent promoting connection of the polymers, that is, under certain conditions, the composite hydrogel may comprise a single-phase system.

The single-phases prediction for hydrogel with nanoparticles has become quite evident. Since interphase boundary in such materials is not distinct, it may comprise a transition layer where a gradual change of properties (transition from properties of phase 1 to properties of phase 2) takes place. As to properties of the phases forming the composite hydrogel, at least one of them must be polymeric hydrogel. In this case, the hydrogel is synthesized from natural ingredients easily assimilated by human body with pronounced positive physiological effect after consumption of such systems.

The second phase, with consideration of interphase interactions, is responsible for morphology of film-forming edible gels. In addition to morphology, other factors (size of structural elements, nature of interphase interactions, methods of obtaining and connection of two phases) are also quite important and may be used as a basis for classification of such systems. It is worth to note that change of dimensions of structural elements may lead to creation of materials consisting of the same ingredients but having principally different properties [9]. As to nature of interactions between ingredients, these interactions may be due to covalent bonds in block- and graft copolymers, forming interpolymer complexes at the expense of appearances of hydrogen bonds, donor/acceptor, ionic and hydrophobic interactions of functional groups, as well as to engagements of macromolecular chains in interpenetrating and semi-interpenetrating polymer networks. The said interphase interactions are directly connected with methods of obtaining composite polymeric hydrogels: connection of polymers in solution and subsequent forming physical or chemical bonds between polymers, co-synthesis or sequential synthesis of polymers accompanied by phase separation [10]. The technological implementations of these two variants are quite various and will be studied in a short time.

There were studied functions of low-molecular weight polyuronate fractions in binding calcium and calcium-induced gelling of normal low methoxyl pectin (LMP). The fractions of pectin with two different degrees of esterification (DE), as well as of alginate with two different mannuronate/ guluronate (M/G) ratios were obtained within molecular-mass range approximately from 40 to 65 kg/mol. In mixtures of LMP and each

fraction of polyuronate, the relative viscosity (η_r) of diluted solutions and rheological properties of gels were studied in presence of calcium. Different results were obtained for pectin and alginate fractions. Addition of pectin fractions, irrespective of their DE, increase of η_r of diluted solutions and increased dynamic storage modulus (G') of gels demonstrated a greater effect for lower DE. On the contrary, addition alginate fractions, irrespective of M/G ratio, increased critical threshold concentration of calcium required for increase of η_r of diluted solutions and decreased G' of gels, demonstrating a greater effect for lower M/G.

Conclusions

It was established that solution on the basis of P:A (pectin/alginate) compositions have properties of non-Newtonian liquids, which viscosity depends on shear stress. For mathematical description of composites behavior, the power-law dependence of Ostwald-de Ville equation is the most suitable since it corresponds to the pseudoplastic fluid model. The correlation of dependence of solutions properties from composition with mechanical characteristics of the films formed from them (rupture strength and elongation) was detected. It was found that content of non-film-forming additives shall be within molecular ratios with consideration of binding points. Otherwise, the mechanical properties of the films deteriorate in a great extent. The water solubility of two-ingredient films and their moisture permeability were determined, and it was shown that the solubility increases in proportion with growth of content of cross-linking agents while growth of moisture permeability is just inconsiderable. The obtained films have a good prospect of use as an edible packaging for many groups of foods.

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АНОТАЦІЯ У статті розглянуто метод синтезу та аналізу фізико-хімічних характеристик гелів харчових плівкоутворюючих на основі композицій уронових полісахаридів, зшитих наночастинками кальцію. Визначено необхідність створення гідрогелів харчових плівкоутворюючих. Досліджено функції низькомолекулярних поліуронатних фракцій в зв'язуванні кальцію і індукованого кальцієм гелеутворення нормального низькомолекулярного пектину. Результати роботи стали науковим підґрунтям для розробки технології харчових покриттів, що самоорганізуються і біодеградують при стандартних умовах.

Ключові слова: гелі харчові плівкоутворюючі; уронові полісахариди; альгінат натрію; низькоетерифікований пектин; іони кальцію; синтезовані композиції.

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