CREEP AND RELAXATION PROPERTIES OF MIXED STARCH AND CARRAGEENAN GELS

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Abstract: The structural network of mixed starch and carrageenan gels with milk is made up of starches macromolecules and carrageenan casein complex, mixed gels with whey has a network of starch and carrageenan complexes with serum proteins. The present work studied the creep properties of mixed soryz starch and caragenen gels with salt and sugar, milk or whey. Carrageenan gels with sodium ions are relatively fragile, but elastic and strength with calcium ions. The addition of sugars leading to the formation of gels and improves mechanical properties of it. In both cases (gel with milk and whey) the modules of elasticity increased with increasing concentration of sucrose and glucose. Fortification of gels structure is due to the stabilizing effect of sucrose and glucose on the ordered structure (spiral) of carrageenan, which is otherwise similar to the effect of salts.

Keywords: starch, carrageenan, creep gel properties, modules of elasticity.

Introduction

In a number of gelled food products (especially those of desert), starch is used as a structure with other hydrocolloids [1].

By hydrocolloid is means diverse functional food ingredients, and particularly, which contributes to the texture, stability and other physical attributes of the processed food. Combined use of hydrocolloids and starch can improve or change the properties of native starch or chemically modified, or may have a synergetic effect [2].

Modification of rheological properties of mixed systems of starch and hydrocolloids is due to the fact that most hydrocolloids are highly hydrophilic substances and compete (along with starch) interactions with water [3].

In the category of natural hydrocolloids shall enter, mainly, polysaccharides compounds and of protein nature (gelatin, caseinates, etc.). Among the compounds of polysaccharide nature special interest presents carageenans. They are linear polysaccharides composed of galactose and anhydro–galactose molecules more or less sulphate [4].

Carrageenans act synergetic with carob bean gum and proteins.

Interest in the use of carrageenan to obtain binary gels of starch and carrageenan was determined that it has a high gelling power (eight times larger than that of gelatin), form gels heat–resistant (up to 65°C), gelation is instantly, does not alter the taste, is widely used in food technology, and in particular milk products. Therefore, as solvent agents were used milk and whey. Have been studied creep and recovery of mixed gels starch (6%) and the κ–carrageenan (0,1 to 0,9%).

In general, the creep property of the material is mean to change over time tense and strain. By tracking the variation of strain over time and through creep curves, creep is determined by defining the corresponding deformation tention equal to unity.

$$F(\sigma_k, t) = \varepsilon / \sigma_k \quad (1)$$

where: **$\sigma\kappa$** – constant effort that confronts sample, kgf/cm^2
ε□ – deformation, %

After discharge (zero), the total deformation will present three distinct areas: instantaneous elastic recovery ($\varepsilon_{\varepsilon}$), retarded elastic recovery ($\varepsilon_{\varepsilon\iota}$), and plastic deformation ($\varepsilon_{\pi\lambda}$). When the curve of creep deformation occurs instantly ($\varepsilon_{\varepsilon\iota}$), it is present on the recovery curve (creep backwards) when tension cancellation. The remaining deformation was recovered slow reverse creep curve tending asymptotically to a constant value, ε_{∞}, named residual deformation. For starch gels are considered as representative Maxwell–Thomson (Zener) model, which emphasizes the instantaneous elastic properties and retarded elasticity.

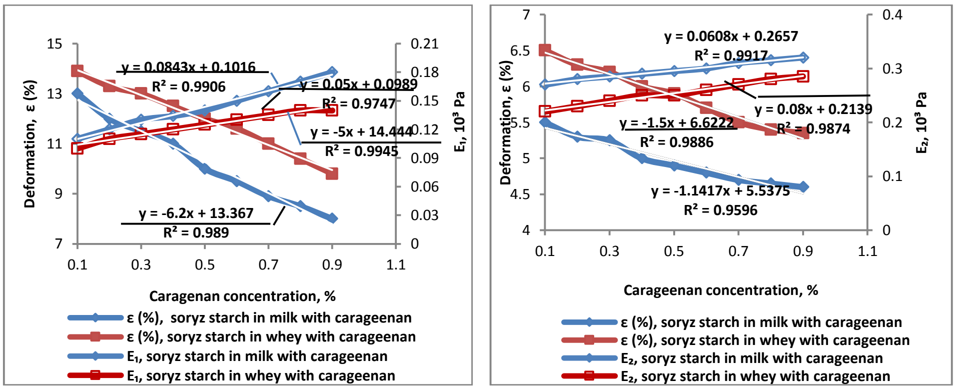
Materials and Methods

Materials: Soriz starch, κ–carrageenan ((PD 14027 – 2e), whey, milk SM 104.

Methods: Creep and relaxation behavior of starch gels. Principle: Determination of irreversible deformation witch increases with time under a constant force [5].

Results and discussion

The results show that the use of milk and whey as a solvent agent and incorporating carrageenan produce a significant increase in the retarded and instantaneous elastic modules of gels and their values increase with increasing content of carrageenan in gels. This indicates the formation of a mixed gel of carrageenan and starch complex resulting from the interaction of starch, carrageenan and / or milk and whey proteins.



a) b)

Fig. 1. The dependence of elastic deformation ε, instantaneous elasticity module (a) and retarded (b) of soryz starch gel in milk and whey on carrageenan concentration

Impact of carrageenan on starch behavior during gelatinization and gelling in water has been studied by M. Sikora (2008) and Baranowska, HM (2008). The authors found that the influence of hydrocolloid is complex and affects swelling and gelatinization of granules and binary gels properties depend on the thermodynamic compatibility of starch with hydrocolloids. They believe that the presence of hydrocolloids affect relaxation time of water molecules, which play an important role in the dynamics of starch gelatinization, formation and structure of gels. The mobility of water molecules initially increases with increasing temperature up to gelatinize the starch then falls due to its immobilization in the formed gel structure. The degree of damage of water mobility and the gelling process, on the one hand, and the network structure of formed gels, on the other hand, depends on the structure and ionic nature of the hydrocolloids. Thus, we can say that carrageenan is involved in intermolecular processes responsible for the formation of network structure of amylopectin, change the matrix and creep properties of the gel. The application of the carrageenan in starch foods, may allow obtaining products with rheological and consumption predetermined properties.

In the case of starch–carrageenan mixed gels, wherein the solvent is milk or whey, an important role plays interactions of carrageenan with solvent proteins (milk casein, albumin and globulins of milk and whey).

Interaction with milk casein results in the formation of a gel at relatively low carageenan concentration compared with required for a aqueous gel [6]. Snoeren et al. (1975) were the first to show that this interaction is electrostatic and occurs between the positive regions of casein (groups of amino acids 97–112) and negative sulphate groups of carrageenan. By electron microscopy studies demonstrated the increase in the diameter of the casein micelles in the presence of k–carrageenan [7].

Interaction of casein micelles with carrageenan occurs only after heating and passage of unordered polysaccharide macromolecules (globular coils) in ordered (linear, spiral).

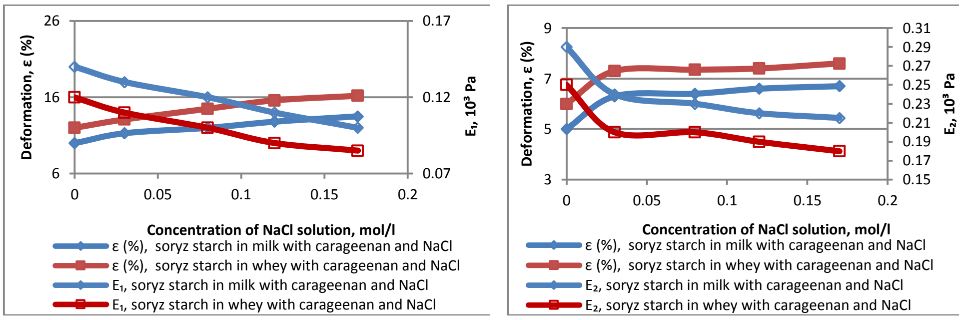
The critical concentration of gelling carrageenan in milk is 0,03%, below which the system remains fluid and casein micelle size increase linearly with the concentration of carrageenan. At higher concentrations they form a three–dimensional network followed by milk gelling [8], casein micelles are trapped within the structural components of the gel.

Undoubtedly, a special role have and the other milk proteins (whey protein), in particular lactoglobulinele, which can interfere with the interaction of casein to carrageenan, but may also form separate the polysaccharide complex.

The results show that heating the mixture of whey starch and carrageenan up to 45 °C and subsequent cooling to 20 °C produces a not homogeneous gel with native serum protein inclusions. The presence of native proteins weakens less density and rheological properties of the gel network. However, if the mixture is heated to 90°C and then cooled, occurs the formation of a complex network's, resulting in a rigid homogeneous gel. This network resulting of electrostatic interactions between carageenan and serum proteins, in particular, β–lactoglobulin, which possesses a positively charged region sequences 76–102 and 126–150 [9].

Salts impact. The presence of sodium monovalent cations and calcium divalent induce changes in the properties of creep and recovery of mixed starch and carrageenan gels. These modifications are based on the concentration of ions in solution (Figures 2 and 3).

Gels deformation with added NaCl increases, and the modules of elasticity decrease with increasing concentration of Na ions up to a certain critical value, after which evolution is reversed. For gels with Ca ions, deformation decreases at low concentrations, up to 0,03 mol/l, and the modules of elasticity, respectively, increase, followed by an increase in the value of deformation. The effect of curing the gel is more pronounced in the presence of Ca ions and less pronounced in the presence of Na ions.



a) b)

Fig. 2. The dependence of elastic deformation ε, instantaneous elasticity module (a) and retarded (b) of soryz starch and carageenan gels in milk and whey on the concentration of NaCl (t = 40 min., $\sigma_\kappa = 1,47*10^3$ Pa)

The mechanism by which cations interact with carrageenan is different.

Sodium ions with positive charge falls within the alveolar structure of carrageenan and thus neutralize the negative charges of sulfuric groups, then it is possible to bring carrageenan macromolecules (there is no electrostatic repulsion) and their association with formation of structural elements in double helix. Namely, the range of high sodium ions hydration prevents its approaching the anion groups, and their neutralization. In general, all alkali metal ions are able to increase the gelling tendency of carrageenan, and their effectiveness is in line with Hofmeister series activities [10].

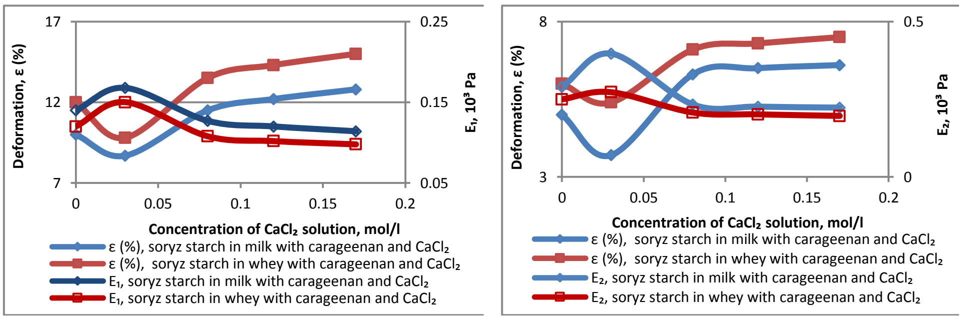


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Fig. 3. The dependence of elastic deformation ε, instantaneous elasticity module (a) and retarded (b) of soryz starch and carageenan gels in milk and whey on the concentration of $CaCl_2$ (t = 40 min., $\sigma_\kappa = 1,47*10^3$ Pa)

Calcium ions (Ca$^{2+)}$ increase rigidity of gels, the maximal effect is at a concentration of about 0,07–0,08 mol/l. The interaction of calcium ions with the carrageenan is the same electrostatic, resulting in the formation of intermolecular bonds (calcium bridges with sulfide groups). Carrageenan gels with sodium ions are relatively weak, strong and elastic with calcium.

Sugars impact. Simple sugars impact on the properties of starch and carrageenan mixed gels in milk or whey is quite difficult to assess quantitatively. That's because sugar changes activity of environment, affects behavior of milk and whey proteins, intervenes both in the starch network structure, as well as that of carrageenan. Creep and recovery characteristics of the carrageenan and starch gels with the addition of sucrose and glucose are presented in Figures 4 and 5.

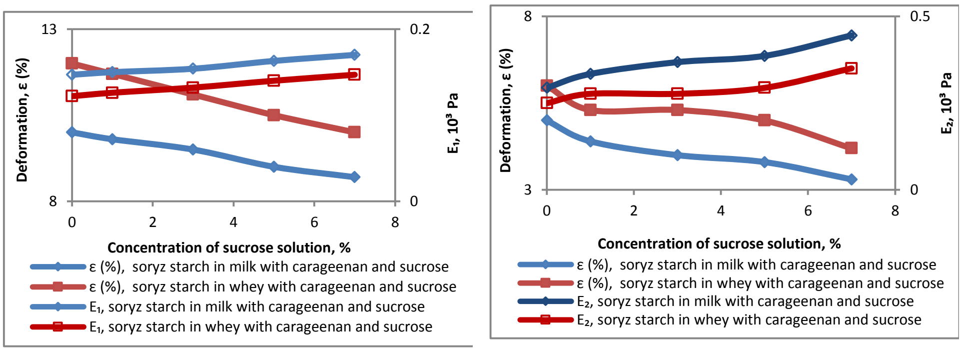

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Fig. 4. The dependence of elastic deformation ε, instantaneous elasticity module (a) and retarded (b) of soryz starch and carageenan gels in milk and whey on the concentration of sucrose (t = 40 min., $\sigma_{\kappa} = 1,47*10^3$ Pa)

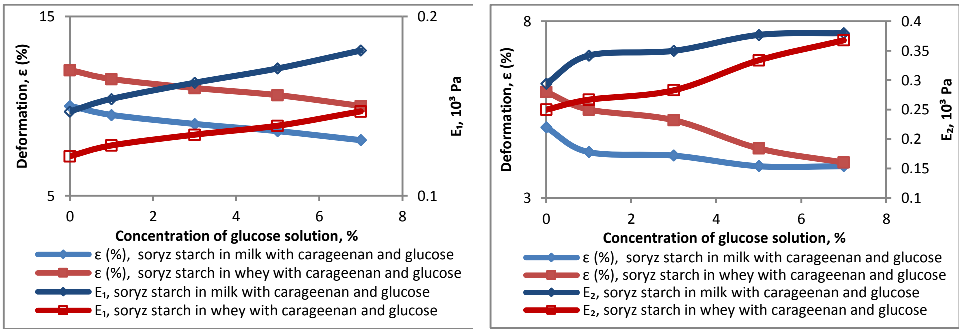

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Fig. 5. The dependence of elastic deformation ε, instantaneous elasticity module (a) and retarded (b) of soryz starch and carageenan gels in milk and whey on the concentration of glucose (t = 40 min., $\sigma_{\kappa} = 1,47*10^3$ Pa)

The sugar can stabilize the conformation of the protein, or may alter the interactions between the protein and the polysaccharide and/or solvent [11]. The sugars change the structural and rheological properties of gels, reinforces casein–casein and casein–polysaccharide interactions. Sucrose and glucose change the temperature of serum proteins, making them more difficult to distort. The presence of sucrose diminishes the water activity inducing an increase in protein–protein and protein–polysaccharide interactions, resulting in the enhancing of the gel network [12].

The results show that the addition of sugars leading to the formation of elastic gels and improves their mechanical properties. In both cases (milk and whey gel) the instantaneous and retarded modules of elasticity increased with increasing the concentration of sugar (sucrose and glucose). It can be assumed that fortification of gels structure is largely due to the stabilizing effect of sucrose and glucose on the ordered structure (spiral) of carrageenan, which is otherwise similar to the effect of salts. In addition, it is possible that the presence of sucrose diminish the water activity of inducing an increase in protein–protein and protein–polysaccharide interactions, also enhancing the gel network.

Conclusions

The structural network of starch and carrageenan gel is mixed, consisting of amylopectin macromolecules (1) and the complex of carrageenan and the casein (2). Formation of casein and carrageenan complexes have a electrostatic nature and occurs after modification (heating) spatial configuration of polymer carbohydrate (globular → linear spiral), which leads to closeness and electrostatic interaction of negative charges of carrageenan groups with positive charge of casein groups. Whey mixtures of starches and carrageenan, also forms mixed gels that have a network of amylopectin (1) and another, complex of carrageenan with serum proteins (2).

The presence of salts and simple sugars in mixed starch and carageenan gels in milk and whey improve creep properties and are important factors to obtain products with desired consumer characteristics and for monitoring theirs physico–chemical and organoleptic properties.

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