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Anomalous properties in aqueous solutions of polysaccharides

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Abstract

Introduction. The study of physicochemical properties of suspensions of polysaccharides in a wide range of mechanical stress and temperature are important in justifying the technological conditions of production of quality food.

Materials and methods. For experiments prepared 0.5% suspension of guar gum, xanthan gum and carob gum, 1.5% suspension of pectin and 10% suspension of native potato starch in distilled water. These suspensions kept in an incubator for 30 minutes at different temperatures in the range 20-90^{0}C.

Results. The existence in diffractograms studied polysaccharides broad band indicates that the dissolution of these substances in water are formed or associates polymer molecules and water. Analysis micrographs of samples polysaccharides confirm this statement. However crystallinity associates gum appears rather weak, which may be associated with features of the structure of the molecules gum with branched side chains. With increasing temperature aqueous solutions of polysaccharides above 400 C is destroyed quasicrystalline structure complex molecules, increases mobility solution, resulting in a disordered structure. This should increase the density of the solution, causing its viscosity to a temperature of 400 C, above which the viscosity begins to decrease. This anomalous behavior solutions can be explained polymorphic transformations polysaccharide molecules in the temperature range 35-55^0 C with increasing freedom of movement, as evidenced by the existence of exothermic peak in differential scanning calorimetry curves.

Conclusion. As a result of polymorphic transformations increases the activity of polysaccharide molecules in intermolecular interactions.

Introduction

In the newest food technologies used natural polysaccharides, which perform the functions: thickening and gelling aqueous solutions, stabilizing foams, emulsions and suspensions, slow crystallization of ice and sugar, regulate taste of food, stability of solutions during heating, transparency, control syneresis, regulation astringents properties, stability, pH and others. Easy to use polysaccharides in different manufacturing processes to create a wide range of quality food products: mayonnaises, sauces, pastes, dairy products, dairy desserts, juices, jellies, jams, salad dressings, meat products, baby foods and dietary foods, bakery products [1, 3, 6, 8, 12, 17, 18, 22, 26, 27]. Permit for the use of natural polysaccharides in the food industry has been provided by the European Commission in 1995 in the framework of Miscellaneous Additives Directive 95/2/EC.

Polysaccharides - water soluble compounds are widespread in nature. By sources of origin and their preparation can be divided into 4 groups: botanical (cellulose, starch, pectin, guar gum, carob gum, et al.), from seaweeds (agar, carrageenan, alginate), microbiological (xanthan gum, dextran, kurdlan et al.), animal (gelatin, casein, chitosan) [4, 12, 28].

Consider especially the preparation and use of certain polysaccharides that are widely used in the production of various food products.

Pectin separated from citrus and apple marc, sugar beet pulp and sunflower baskets. Important biological properties of pectin caused the presence of free carboxyl groups and hidrocarboxyl galacturonic acids. These groups are able to bind heavy metals, including radionuclides to form insoluble complexes that removed from the body.

Pectin also regulates cholesterol, improves intracellular reactions of respiration and metabolism, increases resistance to allergic factors, stimulate wound healing, speeds up the treatment of burns.

Starch - the main reserve polysaccharide of plants that accumulates in the form of granules in the cells of seeds, bulbs, tubers and in leaves and stems. Starch molecules are composed of two polysaccharides: amylose and amylopectin, and their ratio varies widely for different botanical origin of starches. As a result of physical, chemical, biological or combined effects changing the structure and properties of starch, making this polysaccharide is universal in application in the food industry.

Carob and guar gums isolated from the seeds of leguminous plants. Polysaccharide chains have a similar irregular chemical structure with alternate linear and branched zones. The use of these gums in food technology due to the following properties: the ability to form viscous aqueous solutions, synergistic interactions with other polysaccharides, leading to the formation gels of different structure, the ability to regulate the process of syneresis. These gums are not degraded in the gastrointestinal tract of humans and can be used for making baby food.

Xanthan gum is produced during fermentation by bacteria Xanthomonas Campestris with a molecular weight from one to several million. Xanthan is marked by three important properties that provide indispensability of this product: the ability to maintain long dispersed particles in suspension, unique pseudo ductility and resistance to intense mechanical and thermal actions. Use of xanthan gum can provide all the qualities that are necessary foods for success in today's market: stability, desired structure, presentation and natural.

According to modern research [7, 10, 19, 29, 30], polysaccharide molecules have a complex structure and exhibit the ability to form helical chains, where a special role in stabilizing this structure plays water. The behavior of colloidal polysaccharides suspensions in food systems primarily depends on the state of water in the polymer. Branched chain polymers form different structures in space due to the existence of strong hydrogen bonds between water molecules and hydroxyl groups of polysaccharides. Such structures are not stable and may be conformational transitions under mechanical and thermal loads, which can affect the behavior of technological products processing. Therefore, the study of physicochemical properties of suspensions of polysaccharide in a wide range of mechanical stress and temperature are important in justifying the technological conditions of production of quality food.

Materials and methods

The potato starch used in this work is commercially available and was supplied by VIMAL PPCE (Ukraine). The amylose content in the starch used was about 36% (manufacturer's data).

Apple pectin was given by ZPOW "Pektowin" S.A. (Poland), guar gum, carob gum, xanthan gum were obtained from A&Z Food Additives Co., Ltd (China).

For experiments prepared 0.5% suspension of guar gum, xanthan gum and carob gum, 1.5% suspension of pectin and 10% suspension of native potato starch in distilled water. These suspensions kept in an incubator for 30 minutes at different temperatures in the range 20 – 90^{0}C.

Rheological behavior of prepared suspensions, heated at different temperatures, was studied on the «Reotest-2» (Germany) at room temperature.

Prepared specimens were observed using polarized light optical microscopy «Mikmed-6» (Lomo, St-Petersburg Russia).

For the X-ray studies, treated at different temperatures suspension dried at room temperature and crushed.

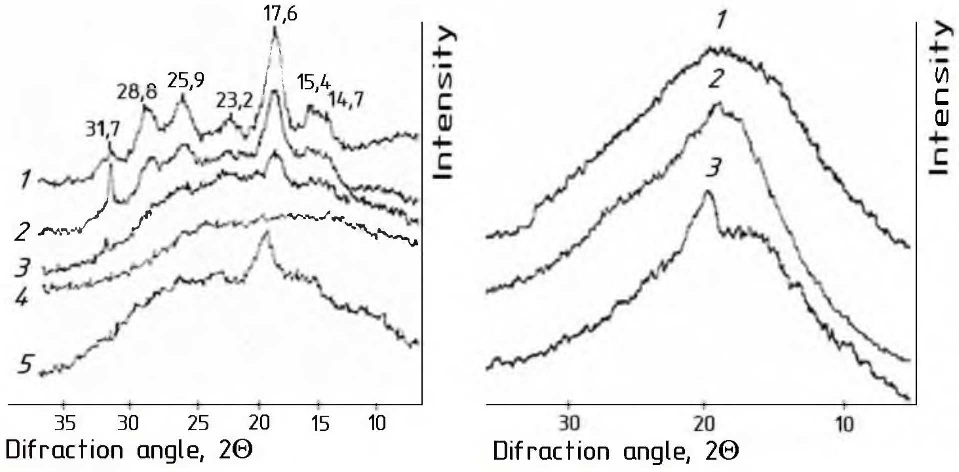
Thermal properties samples were analysed using differential scanning calorimeter DSC Q2000 (TA Instruments, USA). Samples were heated at a rate of 10^{0}C/min from 25 to 100^{0}C.

The X-ray diffraction analysis was performed using a diffractormeter type D8 (Bruker, Germany) under the following conditions: X-ray tube, 36KV and 20mA with 0.1542 nm CuK radiation, the scan rate 4^0/min, scanning from $\theta=5^0 \sim 35^0$, step interval 0.02°, continuous scanning.

Results and discussion

Analysis of the diffraction pattern of a number polysaccharides powders (Fig. 1 A, B) obtained in the paper and in [11, 13, 15, 25, 31, 37], indicating their identity: the background of a strong broad band in the range of 5-35^0 observed narrow lines that are characteristic of partially oriented crystal structures. Most clearly, they are shown for native starches, indicating a high degree of crystallinity of structural elements, which is 20 - 30% [4, 5, 21, 29, 36].

With increasing processing temperatures the crystallinity of aqueous suspensions gradually decreases and disappears completely within the temperature range 70 – 80^{0}C. With further heating the suspension to 90 – 95^{0}C and holding the samples at this temperature for several hours, on the diffraction pattern new narrow band, indicating retrogradation structure of the polymer [5, 14, 16, 21, 34].



a *b*

Figure 1.
a - X-ray diffraction patterns of native potato starch (1) and heat-treated at 60°C (2); 70°C (3); 80°C (4); 90°C (5); b
b - X-ray diffraction patterns of carob gum (1), pectin (2) and guar gum (3).

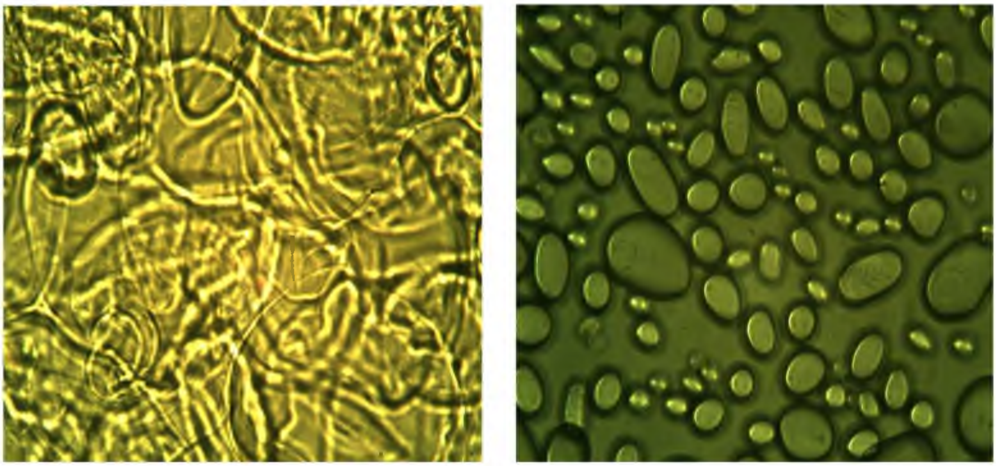
The methods of X-ray diffraction, thermal analysis and NMR spectroscopy [2, 4, 19, 33, 35, 39] shown that native starch molecules are in solution in the form of crystalline starch - water, which melted at 70 – 80°C. This greatly increases activity released from crystalline hydroxyl groups of the polymer to interact with molecules of water and other hydrophilic molecules, in particular the hydrophilic surface of dispersed minerals.

Existence of starch and various gums diffractograms broad band, indicating that when these substances dissolved in water are produced or formed associates polymer molecules and water. Analysis micrographs of samples polysaccharides that shown in Fig. 2, confirm this statement. However crystallinity associates gum appears rather weak, which may be associated with features of the structure of the molecules gum with branched side chains.

Many similar rheological behavior observed in aqueous suspensions of polysaccharides. Thus, depending on the shear strain shear all the samples are typical for non Newtonian fluids even at low concentrations of the polymer [9, 24, 32]. These dependencies can be divided into two areas: at low shear rates is the destruction of intact structure of the polymer solution, and at large - shows much lower viscosity fluid unstructured.

It is important that after the destruction of the polymer solution its structure is gradually recovering. Time to restore it more equilibrium suspensions polysaccharides, such as starch, is 18 hours, whereas for gums 1–2 hours [4]. This confirms the conclusion of a structured solution structure of starch in comparison with gums.

With increasing temperature aqueous solutions, their structure is destroyed, resulting in a decrease viscosity. However, with further increase temperature solutions gums above 40°C an increase viscosity (Fig. 3), and then it gradually decreases.



a *b*

Figure 2. Microphotograph images of potate starch suspensions:
a - native (x 400), *b* - heated to 90^{0}C (x1000).

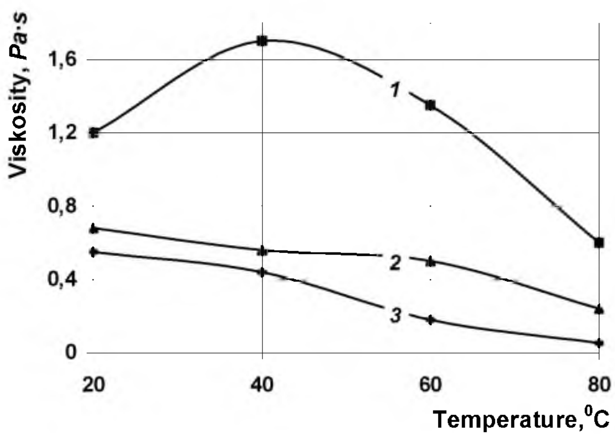


Figure 3. Dependence of the shear viscosity aqueous solutions of polysaccharides: carob gum (1), xanthan gum (2), guar gum (3) on temperature.

This anomalous behavior of solutions can be explained by polymorphic transformations of the gums molecules while increasing freedom of movement, as well as anomalous behavior of water for which the temperature in the range 40 – 60^{0}C observed optimal values physicochemical properties [38].

Conformational conversion of molecules gums also accompanied by thermal effects, as evidenced by the existence of exothermic peak in differential scanning calorimetry (Fig. 4). A similar effect was observed [29] for starch solution, whose value is 10-15 J/g. We can assume, that this exothermic effect is characteristic of all native polysaccharides.

When increasing temperature above ambient viscosity of aqueous solutions decreases. At the same time destroyed quasi-crystalline structure of the complexes molecules that are characteristic of an aqueous mixture of complexes polysaccharides in their structure.

Increased mobility of the solution molecules leads to a violation of this structure and the implementation of polymorphic transformations, giving rise to a more disordered structure. This should increase the density of the solution is increasing its viscosity to a certain temperature, above which the viscosity begins to decrease.

Thus the curve of viscosity on temperature arises optimum specific for each polysaccharide. For comparison, we can cite a famous example of abnormal changes in the density of the water with a temperature where its maximum value observed at 4^{0}C [38]. In both cases, with increasing temperature increases the mobility of molecules, leading to the destruction of quasicrystalline structure solution and reduce its density.

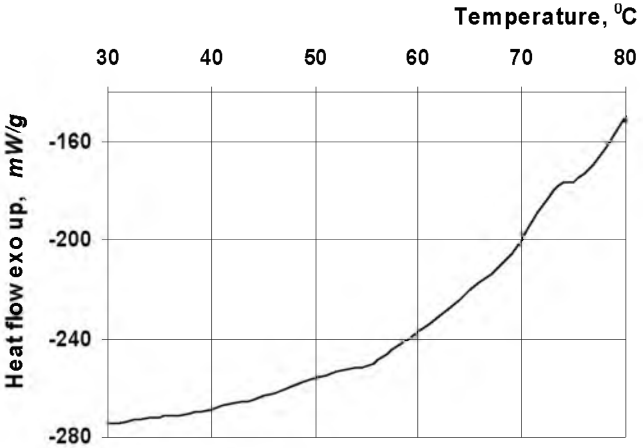


Figure 4. DSC thermograms of guar gum.

Conclusions

The paper studied the viscosity and thermal characteristics in aqueous solutions of polysaccharides carob gum, xanthan and guar gums, pectin, starch in the temperature range 20-90^{0}C.

Established anomalous behavior of viscosity in the temperature range 35-55^{0}C, due to polymorphic transformation structure of biological macromolecules. This conclusion is supported by the existence of maximum thermal effect on the DSC curves.

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