Oksana Tochkova,
Inna Gagan,
Oksana Melnyk

RESEARCH OF THE RHEOLOGICAL PROPERTIES OF WATER VARIANCES OF POLYSACCHARIDES

The object of research is aqueous dispersions of polysaccharides. One of the most problematic factors is the insufficient study and study of the physicochemical properties of polysaccharides, in particular starch. Among natural polysaccharides, starch occupies a unique position. It has a wide range of applications across many industries and technologies. This is what determines a large number of studies of the state of starch of various botanical origin under the action of various factors that have appeared in the literature recently. Natural polysaccharides, in contrast to synthetic ones, are characterized by a partial ordered structure, formed in the process of synthesis and growth.

In the course of the study, a new method of relaxation in starch mixtures was proposed. It was found that structural relaxation in time is slow and long. It was also found that the physicochemical characteristic of polysaccharides, relaxation, is explained by a partially ordered structure with the mutual arrangement of individual chains in a spatial network. It was shown that, under the action of shear stresses, the retest destroys the pseudoplastic liquid structures of aqueous dispersions of starch, followed by restoration to an equilibrium state within 17 hours. The process of recovery or structural relaxation of the spatial structures of aqueous dispersions of polysaccharides occurs due to the rearrangement of the spatial network of the polymer and is formed due to the existence of cross-linked chemical bonds.

Thanks to this method of using polysaccharides, it is possible to obtain improved organoleptic, structural, mechanical and physicochemical characteristics of food products. Compared to similar thickeners (pectin, flour), native potato and corn starches provide and provide structural form to products such as sauces, puddings, pastries, minced meat, fish products, and low fat dairy products. In the food system, the role of polysaccharides is to stabilize structure and interact with other components to deliver or maintain nutrients and taste.

Keywords: *aqueous dispersion of polysaccharides, starch mixtures, shear stress retest, ordered structure.*

1. Introduction

Raw materials, semi-finished products and finished products of the food and processing industry have various structural and mechanical properties, such as elasticity, flexibility, strength, creep, thixotropy, fluidity. These properties of food systems depend on temperature, humidity, pressure, mode of transport, means and storage time. Also, these factors affect the behavior of the structure during its deformation, during mechanical processing: grinding, forming, stamping, etc.

Water quality is also one of the most important indicators that affects the process of obtaining and the quality of food.

In works [1, 2], the dependence of assimilation by the human body of various essential substances from a liquid medium has been studied and investigated. It has been shown that digestibility is an order of magnitude better in a liquid medium than in a solid food. To a large extent, this concerns the set of micro and macro elements contained in natural water.

The main natural chemical composition of water is associated with the mineral components dissolved in it: macro- and microelements. The first – ions of calcium, magnesium, sodium, potassium, chlorides, sulfates, bicarbonates, depending on the predominance of certain substances, determine the hydrochemical class of waters. However, the taste of water can also be due to the presence of trace elements in it, for example, iron, manganese, zinc, copper [3]. The organoleptic properties and especially the taste of water are of great physiological importance for maintaining the water-salt balance of the human body and largely determine the process of its preparation in food production.

For the production of juices, soft drinks, beer, alcoholic beverages, water preparation is required in accordance with strict specific requirements, the main positions of which are set out in the relevant regulatory documents [4]. For a number of food industries, such as bakery products, milk and dairy products, it is sufficient for the water to meet the requirements for drinking water.

The taste of water is primarily due to the content and ratio of calcium and magnesium cations, bicarbonate

ions, as well as the concentration and ratio of sulfates, chlorides and carbonates. These macroelements of water, first of all, determine the physiological usefulness of water for the body. The organoleptic properties of water affect the secretory activity of the stomach, and a change in the taste of water affects the sensitivity of achromatic vision and heart rate [1]. Thus, the content of hardness salts in drinking water in the range of 1–4 mg-eq/l not only improves its taste, but also contributes to the course of normal metabolic processes in the body. With drinking water, a person receives (according to the norms) 1–2 g of mineral salts per day. And due to the fact that, unlike many food products, ions in water are in a hydrated state, their assimilation by the body increases by an order of magnitude.

To improve the organoleptic, structural, mechanical, physicochemical characteristics of food products, polysaccharides are also widely used. They provide some form of foods such as sauces, puddings, pastries, minced meats, fish products, and low fat dairy products. In the food system, the role of polysaccharides is to stabilize structure and interact with other components to deliver or maintain nutrients and taste. For example, polysaccharides can thicken sauces, cream soups, and pie fillings. Colloidal stabilizers for salad dressing, moisture retention for cake. The gel, forming agents for the confectionery gum, binds waffles and ice cream cones, coats and glazes agents for the mass of candies.

Among natural polysaccharides, starch occupies a unique position. It has a wide range of applications across many industries and technologies. This is what determines a large number of studies of the state of starches of various botanical origin under the action of various factors that have appeared in the literature recently. Natural polysaccharides, in contrast to synthetic ones, are characterized by a partially ordered structure that is formed during synthesis and growth. This feature of biological polysaccharide macromolecules is primarily due to their chiral structure, coupled with the existence of hydrogen bonds, including water molecules in their structure [1].

As is known, there is a change in the nature of intermolecular interactions in starch biomacromolecules in the temperature range 40–70 C and its ordered structure is transformed [5, 6]. This is confirmed by experiments in the process of dehydration of gelatinized starch [7].

The structural features of starch are reflected in the rheological behavior of its aqueous dispersions. During processing, starch dispersions will undergo a combination of high heating and shearing, which affects their rheological changes as well as the final characteristics of the product. Subsequent retrogradation will further alter the properties of rheological dispersions. Depending on the source and concentration of starch, the final texture of starchy products will give a thickened solution or gel structure. Thus, the rheological curves of starch dispersions are characteristic of a non-Newtonian fluid, and at low shear stresses the dispersions behave like an elastoplastic system. An increase in tension leads to the destruction of structural formations, and the system behaves like a classical fluid. These properties of the system are due to the presence of intermolecular interactions and chaotic thermal motion of molecules [8–10].

It is assumed that after removing the applied voltage to the system, the initial structure is slowly restored, i. e., relaxation. The relaxation period is characterized by the rate of transition of the system from a non-equilibrium thermodynamic state caused by an external action to a state

of thermodynamic equilibrium. Therefore, it is relevant to study the rheological behavior of aqueous dispersions of starch after a certain period of time after obtaining the next geological curve. Thus, *the object of research* is selected aqueous dispersions of polysaccharides. The *aim of research* is to study the structural behavior of aqueous dispersions of potato and corn starches.

2. Methods of research

For experiments let's prepare a 3–15 % suspension of native potato and corn starches in distilled water. These suspensions are incubated for 30 min at 20 C. The sample is layered in a cylindrical container «Reotest-2» (Germany) at room temperature [11]. After obtaining the rheological curve of the aqueous dispersion of the starch sample, it is left in the retest for 3 hours, after which the rheological curve is obtained.

3. Research results and discussion

In general, shear strain is composed of elastic and viscous components. Elastic components according to Hooke's law [8, 11]:

$$\left(\frac{d\gamma}{d\tau}\right)el = \frac{dP}{(Gd\tau)}, \tag{1}$$

where P – shear stress; G – circular speed.

$$\left(\frac{d\gamma}{d\tau}\right)v = \left(\frac{P}{\eta}\right), \tag{2}$$

where η – viscosity.

Summing up the two components, Maxwell's equation was obtained [8, 11]:

$$\frac{dy}{d\tau} = \frac{dP}{\left(Gd\tau + \dfrac{P}{\eta}\right)}. \tag{3}$$

As is known [12–14], unauthorized restoration of the structure of aqueous dispersions of various substances occurs exponentially. To confirm this model, the rheological behavior of aqueous dispersions of starch was analyzed at regular intervals after the complete destruction of their structure. It is assumed that the value of the shear rate, fixed for each intermediate rheological curve in Fig. 1, at a shear stress of 200 Pa, also changes exponentially depending on the structure of the recovery time.
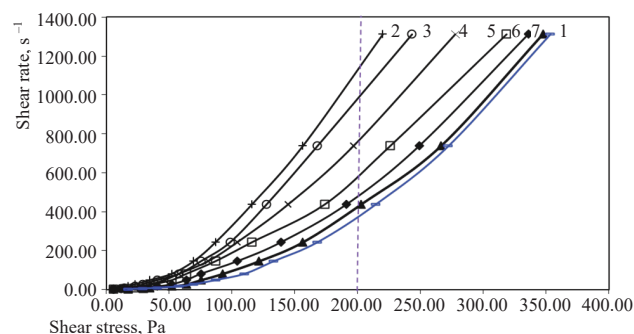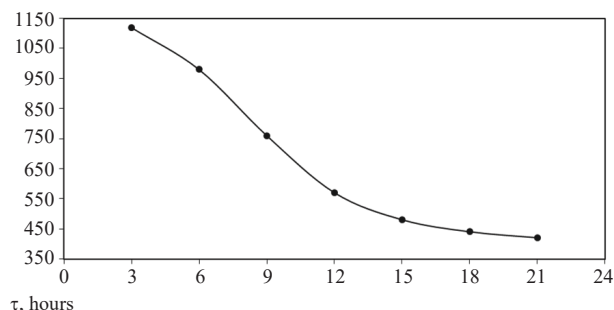

Fig. 1. Dependence of the shear rate on the shear stress for a 5 % dispersion of potato starch, with heat treatment at 20 C (1), measured every 3 hours (2–7)

The time dependence of the shear rate of the starch structure ν at a fixed shear stress of 200 Pa can be represented by the following expression [11]:

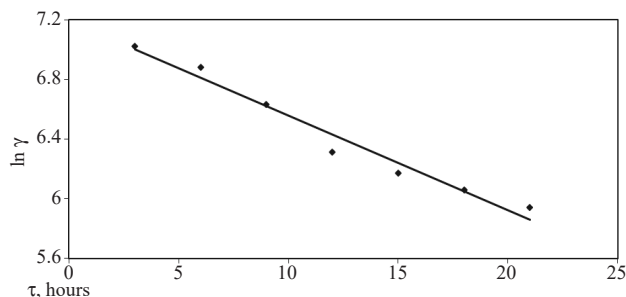$$\gamma = \gamma_0 e^{-\frac{\tau}{\tau_p}}, \qquad (4)$$

where shear rates γ and γ_0 s^{-1}, τ for observation and rest τ_p. Studies to determine 5 % dispersion of potato starch are shown in Fig. 2.

Fig. 2. Dependence of the shear rate on time at a fixed shear stress (200 Pa) for a 5 % dispersion of potato starch heat-treated at a temperature of 20 ℃

To determine the relaxation period, the dependence of the $\eta\gamma$–τ structure is plotted (Fig. 3).

Fig. 3. Dependence of the logarithm of the shear rate (ln γ) on time (τ) at a fixed shear stress

The dependence of the logarithm of the shear rate on time is observed in the equilibrium system shown in Fig. 4. This confirms the proposed mechanism for restoring equilibrium in the system after mechanical excitation. The relaxation rate of the polymer decreases, calculated using equation (1), and is 17 hours. This indicates a very slow process of restoring equilibrium in the system of moving individual polymer units to a more convenient location.

It is natural to assume that the rate of equilibrium restoration will depend on the complexity of the polymer structure. This is confirmed by similar experiments with simpler polysaccharides with a molecular weight of less than 1,000,000, while the molecular weight of starch is 1,000,000. Fig. 4 shows the experimental determination of relaxation in aqueous solutions of xanthan gum. The structural relaxation time of xanthan gum is 210 minutes (Fig. 4).

The relaxation period $\mathrm{tg}\,\alpha = 1/\tau_p$ was calculated as the slope of the line $\ln\gamma = f\tau$. The relaxation period is 17 hours.

The spatial regularities of a very slow relaxation process are characteristic of cross-linked polymers in a highly elastic state, where the relaxation process is caused by the rearrangement of spatial networks formed by intermolecular chemical bonds.
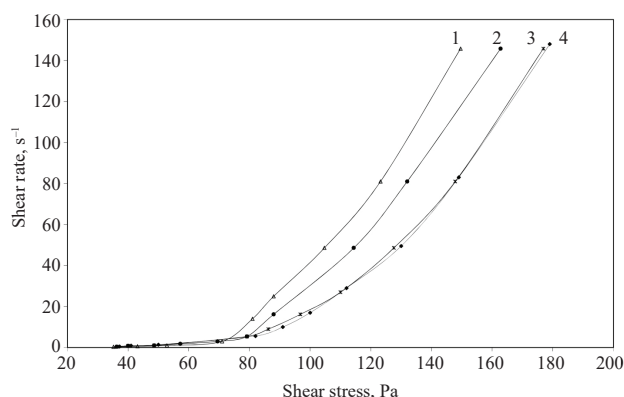
Fig. 4. Rheograms of 5 % xanthan dispersion, heat treated at 70 ℃ (1) and measured every 3 hours (2–4)

In the studied aqueous dispersions of polysaccharides, a similar relaxation of the process is possible, which caused flexible friction over large areas of polymer chains.

4. Conclusions

In the course of the study, the rheological behavior of aqueous dispersions of starch was shown at various stages of restoring the structure of non-Newtonian fluids. Possible models of their relaxation were also considered, and the existence of ordered structures formed during interaction with water molecules surrounding the hydrocarbon chains of biopolymers was confirmed. Under the influence of shear stresses in the rheostat, structural elements in starch mixtures are destroyed. The dispersion system has entered the state of a Newtonian fluid. Rebalancing and returning to its original state in systems is rather slow. A method for changing the time of structural relaxation of polymer carbohydrate chains has been developed. This behavior of aqueous dispersions of polysaccharides must be taken into account when considering the intramolecular interaction and the structure of polymer solutions.

The research results will be useful in the development of technology for the use of polysaccharides as food additives.

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Oksana Tochkova, *PhD, Associate Professor, Department of Canning Technology, National University of Food Technologies, Kyiv, Ukraine, e-mail: tochka-ov@i.ua, ORCID: https://orcid.org/0000-0002-0315-8757*

Inna Gagan, *Assistant, Department of Canning Technology, National University of Food Technologies, Kyiv, Ukraine, e-mail: 2708503@i.ua, ORCID: https://orcid.org/0000-0003-2789-9768*

Oksana Melnyk, *PhD, Associate Professor, Department of Foodstuff Expertise, National University of Food Technologies, Kyiv, Ukraine, e-mail: ksaname@gmail.com, ORCID: https://orcid.org/0000-0002-9177-8904*