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STARCH DISPERSION IN WATER UNDER ULTRASONIC TREATMENT

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Abstract. Decomposition of starch grains in water dispersion and destruction of starch macromolecules in water solutions at acoustic cavitation has been investigated. Kinetics of this process is described by the first order process. Based on experimental data the rate constants have been found. Mathematical model based on found equations and experimental rate constants allows describing the kinetics of starch grains and starch macromolecules destruction in water as well as the change of relative viscosity of starch solution under ultrasonic treatment.

Keywords: destruction, starch, ultrasound.

1. Introduction

Ultrasonic treatment of mineral or organic solid compounds in liquid medium is an effective method to obtain stable dispersions with small size particles and size particle distribution [1-3]. Starch products used in dietetics and medicine to achieve particular technological or physiological properties such as solubility, viscosity properties in solution, swelling and pasting properties, digestibility which are produced from native starches by partial degradation using ultrasound [4]. High molecular compounds are used as stabilizers of particles at the dispersion and at storage of obtained dispersion, but transformation of these polymers under ultrasonic treatment is not investigated well. Ultrasound can be used for disinfection of waste water especially at water pretreatment [5-9] before disperse wastes sedimentation. Low size starch granules with a narrow size distribution can be used in microbiological investigations and starch solutions with narrow molecular weight distribution are promising stabilizers in milk industry [10]. The aim of this article is investigation of the kinetics of organic particle membrane decomposition and destruction of polysaccharide macromolecules solved in water. Dispersion of starch grains in water was chosen as a model for investigations because starch grains allow regulating particle size by previous heating of dispersion to a given temperature.

Surfaces of normal and waxy maize starches were porous after ultrasonic treatment and fissure could be clearly observed on the starch surface [11-13]. Starch amorphous regions and linear amylose degraded more easily than high-branched amylopectin under ultrasonic treatment of gelatinizated starch. Grains swelling in water was destructed under ultrasonic treatment with a formation viscous starch solution [11]. Ultrasonic treatment of corn starch distorts the crystalline region in starch granules [14]. The increase of the swelling power is associated with water adsorption capacity and with starch solubility. Ultrasonic degradation of potato starch paste occurred basing on the mechanism of molecular relaxation of starch paste [15, 16]. There was a random process of molecular mass distribution broad at the initial stage of ultrasonic degradation. After that, ultrasonic degradation of potato starch paste changed to a nonrandom process and the molecular mass distribution became narrower. The goal of this research is to investigate the possibility of obtaining starch dispersion with narrow grain size distribution and water starch solution with narrow molecular weight distribution under ultrasonic treatment of starch dispersion.

2. Experimental

Commercial potato starch produced by Kolos Factory with the water content 12 %, hydroxyl ethyl cellulose with substitution degree 0.74 and molecular mass $5.56{\cdot}10^4$ was used for experiments. Starch dispersions with concentrations 1–2 % were treated by ultrasound in 80 ml tube cooled by water using apparatus UZDN-2T with magnetostrictor and frequency of 22 kHz.

Temperature of dispersion was 298±3 K. The samples of starch dispersions were placed on basic glass of microscope MIN-5 produced by OMO (Russia) to prepare the microphotographs. More than 200 starch grains were used to obtain distribution curves of starch grain sizes. Concentration of starch macromolecules in water solution was investigated by measuring optical density of starch solutions complexes with iodine in the range of wavelengths from 400 to 430 nm using the colorimeter FEK-M (Zagorsk, Russia). The change of the radius of swelling starch macromolecule associates dispersing the light was estimated using the dependence [17]:

$$S = \frac{\Delta \log A}{\Delta \log l} \qquad (1)$$

where $\Delta\log A$ is the change of logarithm of optical density of starch treated by ultrasound at the change of the wavelength, λ, from 300 to 600 nm.

The radius of macromolecule associates can be estimated according to equation [17]:

$$R \sim S^{-2} \qquad (2)$$

Samples of starch dispersion were centrifuged at 8000 s^{-1} for 0.5 h and the starch solution was isolated from the precipitate. Complexes were obtained by mixing of 9 ml of starch solution with 1 ml 0.01 N iodine solutions. Starch solutions were diluted several times before complex formation when optical density of initial complex was more than 0.9. Viscosity of starch solutions in water was measured at 298 K using Bishop viscosimeter. Five or six different concentration solutions of one starch sample were used to determine intrinsic viscosity of starch macromolecules in the solution. Samples of 1–2 % starch dispersion were heated at 313, 333, 353 and 373 K for 0.5 h before investigation of ultrasonic treatment influence on their properties.

Molecular mass distribution was determined by gel-chromatography of starch samples heated at 353 K for 0.5 h using equipment of Waters Corporation with a refractometric detector Waters 2410, pump Waters 515 HPLC and column Ultrahydrogel 500 with sizes 7.8x300 mm. Distilled water was used as a diluent for water soluble starch fraction, and DMSO as a diluent for starch fraction solved in DMSO, at rate 0.1 ml/min. Starch samples dispersed in water were centrifuged at 8000 s^{-1} for 1 h. Water solution above the residue was investigated, the residue was dissolved in DMSO and centrifuged by the same manner and the solution was investigated.

3. Results and Discussion

Starch grains in water dispersion at room temperature are stable and they do not evolve starch macromolecules into the solution during several hours. Investigation of starch grains behavior in water dispersion under ultrasonic treatment shows that starch macromolecules appear in the water solution during several minutes from the process beginning (Fig.1, curve 1).

Linear dependence of starch concentration on time in semilogarithmic coordinates at the initial stage of the process suggests the first order process according to the starch (Fig. 2).

Heating of the starch dispersion leads to swelling of starch grains and to increasing of their volume. The rate of starch macromolecules evolved from its grains rises with the increase of previous dispersion heating temperature. It is needed to note that some quantity of starch macromolecules is present in the solution after dispersion heating at the temperature higher than 313 K (Fig. 1, curve 3). Correlation coefficients of straight lines (Fig. 2) and first order rate constants calculated from the tangents of the slope angles of straight lines are represented in Table 1.

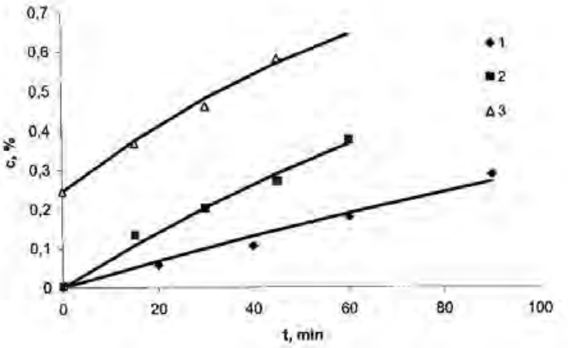

Fig. 1. Dependence of the concentration of starch macromolecules evolved from grains into water on time at ultrasonic treatment of starch dispersion previously heated at 293 (1), 313 (2) and 333 K (3). Theoretical curves calculated according to the Eq. (3)

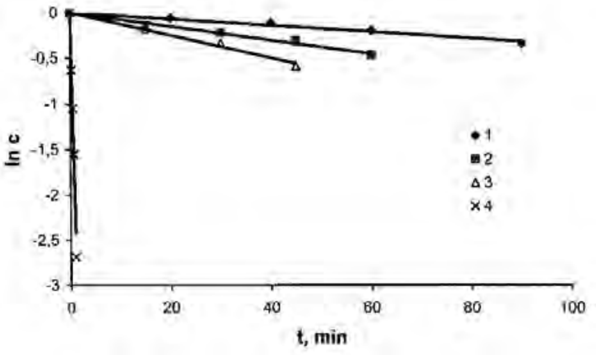

Fig. 2. Semilogarithmic anamorphous of dependence of the concentration of starch macromolecules evolved from grains into water on time at ultrasonic treatment of the starch dispersion previously heated at 293 (1), 313 (2), 333 (3) and 353 K (4)

Table 1

Correlation coefficients and rate constants of the process of starch macromolecules evolved from grains under ultrasonic treatment

Temperature of previous heating, K	Initial concentration of starch macromolecules in the solution, %	*R*	k_1, min^{-1}
294	0	0.986	$(3.5\pm0.2)\cdot10^{-3}$
313	0	0.991	$(7.6\pm0{,}6)\cdot10^{-3}$
333	0.23	0.992	$(1.25\pm0.07)\cdot10^{-2}$
353	0.64	0.979	2.45 ± 0.12

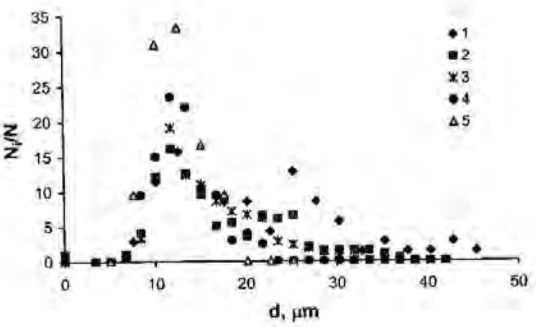

Fig. 3. Distribution of starch grain sizes for initial starch (1), and starch after 15 (2), 30 (3), 45 (4) and 60 min (5) of starch dispersion treatment by ultrasound

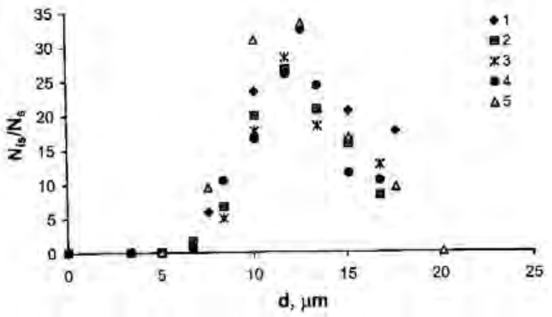

Fig. 4. Distribution of starch grain sizes in the field 5–17 µm for initial starch (1), and starch after 15 (2), 30 (3), 45 (4) and 60 min (5) of starch dispersion treatment by ultrasound

Theoretical curves calculated according to the Eq. (1) taking into account obtained constants describe experimental data quite well (Fig.1).

$$c = c_0 \times \exp(-k_1 t) \quad (3)$$

Change of the starch grain size distribution during the ultrasonic treatment was investigated to find the peculiarities of the grain destruction process by ultrasonic cavitations. Fig. 3 shows that the shape of grain size distribution changes in time: the number of grains with size till 17 µm increases and the number of grains with size more than 17 µm decreases during ultrasonic treatment at room temperature till zero after 1 h.

Therefore, great size grains destruct effectively under ultrasonic treatment but the behavior of small grains is not determined. Some information about the destruction of small size grains during ultrasonic treatment can give the size distribution change of grains with size till 17 µm without taking into account great grains. Fig. 4 shows that the shape of small size grain distribution does not change practically during the whole process. The destruction rate of small grains is evidently very small or they are not destroyed at all. Ratio change of starch grains number with the size greater than 17 µm in the unit volume of dispersion to their initial number in the unit volume can be calculated taking into account the fact that the number of grains with the size lower than 17 µm is practically constant during ultrasonic treatment.

Part of small size grains (4) and part of great size grains (5) are equal to:

$$w_s = N_s / N \quad (4)$$

$$w_g = N_g / N \quad (5)$$

where N_s and N_g are numbers of starch grains less than 17 µm and greater than 17 µm in the unit volume of the dispersion; *N* is the whole number of grains in the unit volume of the dispersion.

One can obtain at initial conditions:

$$w_{s0} = N_{s0} / N_0 \quad (6)$$

$$w_{g0} = N_{g0} / N_0 \quad (7)$$

where N_{s0} and N_{g0} are initial numbers of starch grains less than 17 µm and greater than 17 µm in the unit volume of the dispersion; N_0 is the initial number of different size grains in the unit volume of the dispersion.

Equation (8) can be obtained from Eqs. (4)-(7).

$$N_g / N_{g0} = w_g w_{s0} /(w_s w_{g0}) \quad (8)$$

Grains must destruct according to the first order process if the increase of starch macromolecule concentration in the solution during ultrasonic cavitations is the first order process. Fig. 5 shows that the data change of the ratio N_g/N_{g0} in time is linear in semilogarithmic coordinates. Correlation coefficient of the straight line equals to 0.958 and the rate constant equals to $(4.87\pm0.16)\cdot10^{-2}$ min^{-1}.

Viscosity investigation of the previously heated at 353 K starch dispersion during ultrasonic cavitation shows (Fig. 6, curve 1) that the dispersion viscosity growth during the first two minutes reaches maximum and then decreases.

Viscosity growth can be explained by the destruction of starch grains and solving of starch macromolecules in water. It can be confirmed by the optical density change of starch dispersion during ultrasonic treatment (Fig. 7, curves 1, 2).

Optical density increases at the first stage as the result of extraction and swelling of starch macromolecule associates from grains and then optical density decreases when macromolecules destruct and dissolve in water. Average radius of macromolecule associates rises during 10 min reaching maximum (Fig. 7, curve 3) and diminishes at the second stage. Viscosity decrease after maximum (Fig. 6, curve 1) is evidently resulting from starch macromolecule destruction at ultrasonic cavitations. Molecular mass distribution of starch extracted by water from starch dispersion heated at 353 K (Fig. 8, curve 1) is close to the described one in [18].

Average molecular mass of starch extracted by DMSO is lower than the first one but its content in dispersion is higher (Table 2).

Molecular mass of starch extracted by water and DMSO after ultrasound treatment is lower than the initial samples and their polydispersity is narrower than in the first case. It is needed to note that the content of water soluble fraction of starch is higher after ultrasound treatment than in the initial dispersion. Change of optical density of starch dispersion during ultrasound treatment suggests it (Fig. 7). Viscosity of previously gelatinized starch at 373 K in water decreases from the start of ultrasonic treatment. Intrinsic viscosity of starch macromolecules describing the volume of swelling starch macromolecules decreases too. Linear dependence of intrinsic viscosity logarithm on time suggests destruction of starch macromolecules at ultrasonic cavitations (Fig. 9).

It should be noted that the rate constant of starch macromolecule destruction is close to one for destruction of linear polysaccharide, hydroxyl ethyl cellulose. Correlation coefficients and rate constant are represented in Table 3.

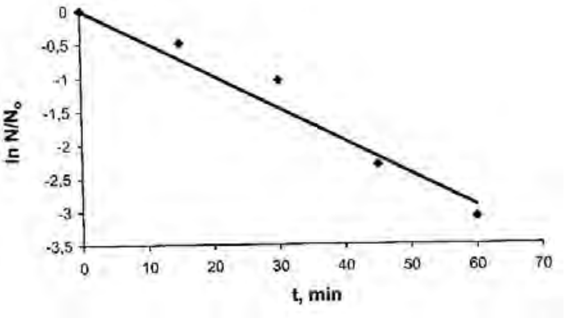

Fig. 5. Semilogarithmic anamorphous of dependence of the number of starch grains with size greater than 17 μm in the unit volume of the dispersion on time at ultrasonic treatment of starch dispersion

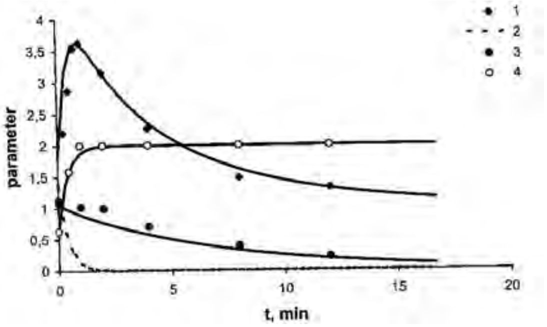

Fig. 6. Dependence of the relative viscosity of starch solution (1), mass of starch grains in the unit volume of the dispersion (2), intrinsic viscosity of starch macromolecules (3) and the concentration of starch macromolecules in the solution (4) on time for starch dispersion previously heated at 353 K under ultrasonic treatment. Theoretical curves were calculated according to Eqs. (9)-(12)

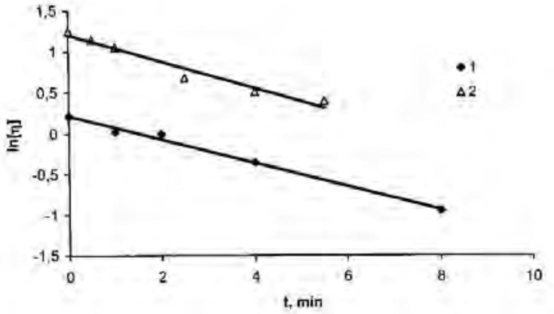

Fig. 7. Change of optical density (1, 2) and radius (3) of starch macromolecule associates on time at ultrasound treatment of starch dispersion previously heated at 353 K

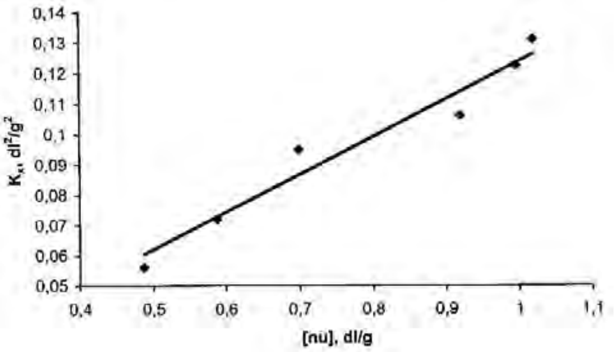

Fig. 8. Molecular mass distribution of starch heated at 353 K and extracted by water (1), by DMSO (2) and after its ultrasonic treatment during 30 min and extracted by water (3) and DMSO (4)

Table 2

Characteristics of starch heated at 353 K and after 30 min ultrasonic treatment

Starch	Content from initial, %	M_w	M_n	Polydispersity
Heated at 353 K and solved in water	12	$3.62 \cdot 10^{6}$	$9.33 \cdot 10^{4}$	38.8
Heated at 353 K and solved in DMSO	56	$1.78 \cdot 10^{6}$	$9.23 \cdot 10^{4}$	19.2
After ultrasonic treatment and solved in water	71	$7.50 \cdot 10^{5}$	$1.54 \cdot 10^{5}$	4.87
After ultrasonic treatment and solved in DMSO	26	$5.53 \cdot 10^{5}$	$9.76 \cdot 10^{4}$	5.66

Table 3

Correlation coefficients and rate constants of starch and hydroxyethyl cellulose macromolecules destruction at ultrasonic treatment

Substance	Measured parameter	R	k, min^{-1}
Starch	$[\eta]$	0.958	0.162±0.008
Hydroxyethylcellulose	$[\eta]$	0.991	0.217±0.006
Starch*	$[\eta]$	0.995	0.190±0.004
Starch*	M_m	0.983	0.173±0.007

*Values were calculated according to experimental data from [15]

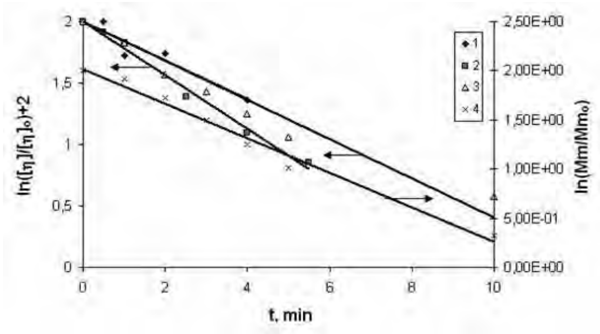

Fig. 9. Semilogarithmic anamorphous of intrinsic viscosity dependence on time for starch macromolecules (1, 3), hydroxyl ethyl cellulose macromolecules (2) and of starch molecular mass (4) in water solution at ultrasonic treatment. Curves (3, 4) were calculated according to experimental data described in [15]

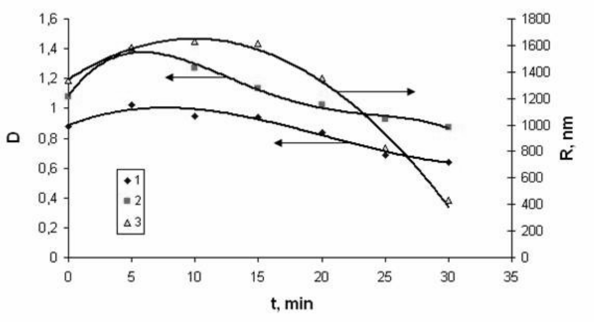

Fig. 10. Dependence of the coefficient K_x in the Eq. (13) on intrinsic viscosity of starch in water

Obtained experimental results allow describing the process of starch grain behavior in water dispersion under ultrasonic treatment. The change of the number of starch grains in the unit volume of dispersion in time can be described by the equation:

$$N = N_0 \exp(-k_2 t) \tag{9}$$

where N and N_0 are grain number and initial number of grains in the unit volume of dispersion; k_2 is the rate constant of starch grain destruction.

Change of a starch macromolecule concentration in the solution during ultrasonic cavitations is described by the equation:

$$c_w = c_{w0} + ((c_0 - c_{w0}) - (c_0 - c_{w0})\exp(-k_1 t)) \tag{10}$$

where C_{w0} is the concentration of starch macromolecules evolved in water solution at previously heating of starch dispersion; C_0 – is the initial starch concentration including starch macromolecules in starch grains and starch macromolecules evolved in water solution at previously heating; k_1 is the rate constant of the process of starch macromolecules evolution from starch grains during ultrasonic treatment.

$$[h] = \frac{c_{wi} - c_{wi-1}}{c_w}[h]_0 + \frac{c_{wi-1}}{c_w}[h]_0 \exp(-k_3 t) \tag{11}$$

where $[\eta]$ is the average intrinsic viscosity of starch macromolecule in water solution in time t; $[\eta]_0$ is the initial intrinsic viscosity of starch macromolecules in water; $(C_{wi} - C_{wi-1})/c_w$ is part of starch macromolecules evolved in water solution from grains at ultrasonic treatment during period of time from t_{i-1} till t_i; C_{wi-1}/C_w is the part of starch macromolecules destructed in water solution under ultrasonic treatment during time t_{i-1}; k_3 is the rate constant of starch macromolecules destruction in water solution under ultrasonic cavitations.

Relative viscosity of starch solution was calculated according to the Eq. (12) taking into account the fact that the viscosity of starch grains dispersion is much less than the viscosity of starch macromolecule solution.

$$h / h_s = \exp([h]c - K_x c^2) \qquad (12)$$

where η and η_s – viscosity of water and starch solution; K_x is constant in the equation:

$$\ln(h / h_s) / c = [h] - K_x c \qquad (13)$$

Value dependence of K_x, calculated according to the Eq. (13) and using experimental data, on the $[\eta]$ is linear in the field of investigated starch solution concentration (Fig. 10). Correlation coefficient of the straight line equals to 0.958 and the tangent of the angle of the straight line equals to 0.124±0.008 dl/g.

Fig. 6 shows that theoretical curves calculated according to Eqs. (9)-(12) describe quite well experimental data on the change of the starch grains number in the unit volume of dispersion, concentration of starch macromolecules in water solution, intrinsic viscosity of starch macromolecules and relative viscosity of starch solution in water on time.

4. Conclusions

Ultrasonic treatment of water starch dispersion enables to obtain starch dispersion with a narrow grain size distribution and starch solution with narrow molecular mass distribution. Rate constants of starch macromolecules evolution from starch grains in the solution has been found at 293–353 K. The destroying rate of starch grains with sizes from 17 till 25 μm under ultrasound treating has been determined. Rate constant of starch macromolecules destruction has been calculated based on the change of the starch intrinsic viscosity under ultrasound treating. Mathematical model based on found equations and experimental rate constants permit to describe the kinetics of starch grain and macromolecule destruction in water as well as the change of relative viscosity of the starch solution under ultrasonic treatment.

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УЛЬТРАЗВУКОВА ОБРОБКА ВОДНОЇ ДИСПЕРСІЇ КРОХМАЛЮ

Анотація. *Кінетика процесу деструкції крохмальних зерен у водній дисперсії і руйнування макромолекул крохмалю в водних розчинах при акустичній кавітації описується рівнянням першого порядку. Наведена математична модель, яка описує кінетику деструкції зерен та макромолекул крохмалю у воді, а також зміну відносної в'язкості розчину крохмалю при ультразвуковій обробці.*

Ключові слова: *руйнування, крохмаль, ультразвук.*