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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Prediction of the Dispersity of Ultrasonically Treated Starch Hydrogels

N. V. Losev and I. M. Lipatova

Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia

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Abstract—Expressions for calculating the expected particle size of the colloid phase and the gain in the content of the water-soluble fraction in starch hydrogels upon their ultrasonic treatment were obtained.

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Gelatinous starch materials are widely used in various branches of industry (textile, food, paper, building). To make starch hydrogels technologically applicable, they are subjected to thermal or thermochemical treatment to break down their primary structure formed by swollen starch grains. Ultrasonic treatment of gelatinized starch allows the time and power consumption for the breakdown of starch grains to be considerably reduced, and the level of the hydrogel dispersity attained in the process cannot be reached by traditional thermal treatment. Strong acoustic fields in liquid media can be generated both by common ultrasonic apparatus and by hydroacoustic devices, in particular, by rotary-pulse apparatus [1, 2]. Wide use of technologies involving ultrasonic or hydroacoustic treatment of gelatinized starch is restricted by the insufficiency of the theoretical basis and lack of reference experimental data for calculation and construction of apparatus ensuring the required level of dispersity of starch hydrogels at minimal power consumption.

The goal of this study was to obtain mathematical expressions for calculating the expected size of colloid particles in ultrasonically treated starch hydrogels from the amount of the acoustic energy absorbed.

EXPERIMENTAL

Experiments were performed with corn starch [GOST (State Standard) 7697–82]. Starch hydrogels for the subsequent ultrasonic treatment were prepared by cooking starch suspension on a water bath at 90°C for 15 min.

Starch hydrogels of the concentration in the range 1–8 wt % were subjected to ultrasonic treatment in a UZDN-2T disintegrator at f = 22 kHz. The exposure time was from 5 to 60 s. The volumetric density of the acoustic energy determined calorimetrically was 1.34 W cm^{-3}.

The content of the water-soluble fraction of starch (A, %) was determined by hot extraction, and the composition of extracts, spectrophotometrically using complexation with iodine [3].

The size of colloid particles in starch hydrogels was determined by turbidimetry from the plot of the logarithm of the optical density on the logarithm of the wavelength, as described in [4]. The refractive indices of the solutions, required for the calculation, were measured with an IRF-22 refractometer. The optical densities of the solutions were measured with a Spekol-221 spectrophotometer.

The initial starch hydrogels are dispersions in which swollen starch grains are distributed in a solution of the water-soluble fraction. As reported previously [5], ultrasonic treatment of starch hydrogels leads already in the first seconds to a decrease in their viscosity and optical density and to an increase in the soluble fraction content. Microscopic studies showed that this is due to breakdown of starch grains.

In ultrasonic disintegration of particles only a minor fraction of the acoustic energy imparted to the material

is consumed by mechanical work. This fraction, E_m (J), is determined as

$$E_m = W_{ac}\eta_m t, \quad (1)$$

where W_{ac} is the acoustic power (W); η_m, erosion-acoustic efficiency; and t, treatment time (s).

In any kind of disintegration, the mechanical energy is consumed for cleavage of intermolecular bonds, and essentially for the formation of a new surface. The relationship between the imparted mechanical energy and the newly formed surface area was suggested by Margulis [6]:

$$E_m = \frac{\Delta S q_0}{2a^2 N_A}, \quad (2)$$

where q_0 is the energy of the bond cleavage per mole of substance (J mol^{-1}); a, kinetic diameter of the molecule (cm); and N_A, Avogadro number (mol^{-1}).

Formula (2) for calculating the mechanical energy of disintegration is applicable only to a few substances for which the bond cleavage energies q_0 are known. For crystalline substances, these are the crystal lattice energies or energies of sublimation. The fraction of the acoustic energy converted to the mechanical work (the erosion-acoustic efficiency η_m) was determined with suspensions of a powdered reference substance with the reliably known energy of intermolecular interaction. The reference substance should meet a number of requirements. It should be insoluble in water and should form stable aqueous suspensions with the particle size close to that of swollen starch grains. It should also undergo ultrasonic disintegration under the experimental conditions.

Crystalline benzoic acid (melting point 122°C, energy of intermolecular interactions E_m = 89.5 kJ mol^{-1} [7]) meets all these requirements.

The specific surface area of the initial and ultrasonically treated benzoic acid powders was determined by computer processing of a series of photomicrographs, with the particles approximated by rectangular bars and cubes. For the initial sample, we simultaneously measured the specific surface area by ammonia adsorption. Both methods gave close results.

After substituting the experimental and literature data in formulas (1) and (2), we calculated the mechanical energy spent for disintegration of benzoic acid particles and the erosion (or mechanical) efficiency η_m, which appeared to be equal to 0.042%.

For the mathematical description of the disintegration process in starch hydrogels, we assumed that the newly formed surface area is equal to the total surface area of all the particles formed. The initial surface area of the intact grains can be neglected, because it is smaller than the area of the newly formed surface by two orders of magnitude on the average.

Analysis of data on the kinetics of ultrasonic cleavage of starch [5] and of the results of microscopic studies allows a conclusion that cavitation disintegration of starch hydrogels occurs by the mechanism of instantaneous cleavage of grains to spherical, conventionally equilibrium particles of finite size (Fig. 1).

To simplify the calculations, we assumed that the total volume of particles formed from one grain is equal to its volume. Hence follows that the number of particles n_p of diameter d formed from one grain of diameter D_g is equal to the ratio

$$\sum_{i=1}^{n} \frac{\pi d^3}{6} = \frac{\pi D_g^3}{6} \longrightarrow n_p = \frac{D_g^3}{d^3}. \quad (3)$$

The number of grains in volume V (cm^3) of the initial starch hydrogel subjected to treatment can be determined by the formula

$$N = \frac{6cV}{100\rho_d \pi d_d^3}, \quad (4)$$

where ρ_d is the density of the dry starch grain, ρ_d = 1.45 g cm^{-3} [8]; d_d is the diameter of the dry starch grain, for corn starch $d_d = 15 \times 10^{-4}$ cm; c is the starch concentration in the hydrogel (wt %).

Then the total surface area of particles S (cm^2) formed in volume V of the gel will be equal to

$$S = \pi d^2 \frac{D_g^3}{d^3} \frac{6cV}{100\rho_d \pi d_d^3} = \frac{0.06c\alpha^3 V}{\rho_d d}, \quad (5)$$

where $\alpha = D_g/d_d$ is the degree of swelling of grains.

Here we should take into account a specific feature of starch pasters consisting in a decrease in the degree

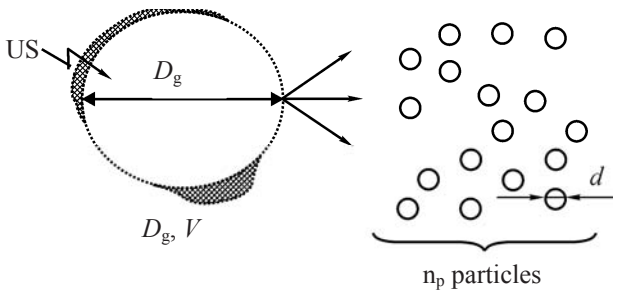

Fig. 1. Scheme of cleavage of a swollen starch grain.

of grain swelling α with an increase in the starch concentration after reaching a certain critical point c_c at which the swollen grains come in contact. Depending on the starch batch and cooking conditions, c_c can vary from 3.5 to 4.2 wt %. This concentration can be determined more accurately for specific conditions from the bend in the concentration dependence of the viscosity, plotted in log–log coordinates. Provided that the initial shape of grains is preserved in the course of swelling, their volume fraction φ at various $c > c_c$ should remain constant, and an increase in the concentration should be accompanied only by the corresponding decrease in the diameter of swollen grains. The closest packing of monodisperse spherical particles is characterized by φ = 0.74 [9]. After relatively simple mathematical transformations, we obtain a formula for calculating the degree of swelling for various starch concentrations c_i in the hydrogel:

$$\alpha_i = \sqrt{\frac{100\rho_d\varphi}{c_i}} = \frac{4.75}{\sqrt[3]{c_i}}. \quad (6)$$

Thus, formula (5) for calculating the total surface area of particles is applicable only to starch concentrations that do not exceed c_c. For $c > c_c$, this formula is simplified to

$$S = \frac{6\varphi d}{d}. \quad (7)$$

In formula (2), the parameter a^2 is defined as the area per contacting unit. The contacting unit in dry starch is the glucopyranose ring ($a = 0.5 \times 10^{-7}$ cm). On swelling in the course of gelatinization, the grain cross section area increases by a factor of D_g^2/d_d^2. Therefore, in formula (2) instead of a^2 we should write $a^2\alpha^2$. Then, using modified formula (2) and formula (1), we obtain an expression for calculating the conventional bond energy q_0 for gelatinized starch:

$$q_0 = \frac{W_{ac}t\eta_m 2a^2\alpha^2 N_A}{S}. \quad (8)$$

In ultrasonic treatment of starch hydrogels of concentration 3 wt %, complete cleavage of grains was attained in 10 s. The treated samples were subjected to turbidimetric examination. In three replicate runs, we obtained reasonably consistent values of the particle size of cleaved starch hydrogel d, equal to 2 μm on the average. Using the total surface area calculated by formula (5), we obtained q_0 from the results of a series of experiments. The mean value of q_0 for gelatinized starch was 9.1 ± 0.5 kJ mol^{-1}.

The quantity q_0 characterizes the stability of swollen grain to mechanical disintegration. This is an integral quantity including all factors that counteract the grain cleavage (intermolecular interaction, stabilizing effect of lipid shell, effect of interphase tension). The resulting value of q_0 is of the same order of magnitude with such known experimental energy characteristics of starch as the energy of hydration of OH groups, equal to 8.47 kJ mol^{-1} per group [10], and energy of intermolecular interaction via nonpolar groups, equal to 12.2 kJ mol^{-1} [11]. The quantity q_0 can be used for calculating the expected degree of dispersity, i.e., the size of colloid particels d, in ultrasonic disintegration of starch paster, taking into account its concentration and amount, and also the acoustic power. Using Eqs. (1), (2), and (5)–(7), for two regions of starch concentrations in hydrogels we obtained the following formulas for calculating the expected particle size in mechanically cleaved hydrogels d (cm):

$$d = \frac{0.06q_0}{2a^2\rho_d N_A}\frac{\alpha cV}{W_{ac}t\eta_m}, \; c < c_c, \quad (9)$$

$$d = \frac{0.06\varphi q_0}{2a^2 N_A 22.56}\frac{c^{-2/3}V}{W_{ac}t\eta_m}, \; c > c_c. \quad (10)$$

In serial experiments, to estimate the attained level of dispersity in starch hydrogels we can use the gain in the water-soluble fraction content ΔA (%).

The amount of starch Δm (g) that passed into solution during the time of ultrasonic treatment in volume V (cm^3) of starch paster of concentration c (wt %) will be equal to

$$\Delta m = \frac{\Delta AcV}{10^4}. \quad (11)$$

As shown in [12], the quantity Δm is linearly related to the newly formed surface area:

$$\Delta m = \Delta S \Delta m_s,$$

where $\Delta m_s = 1.6 \times 10^{-7}$ g cm^{-2} is the experimental proportionality coefficient.

This quantity was used for calculating the expected gain in the starch soluble fraction Δm, characterizing the extent of ultrasonic disintegration of grains, from the imparted acoustic energy:

$$c < c_{cr}: \Delta m_{ac} = W_{ac}\eta_m t\alpha^2 \text{const}, \quad (12)$$

$$c > c_{cr}: \Delta m_{ac} = W_{ac}\eta_m t 22.56 c^{-2/3} \text{const}, \quad (13)$$

$$\text{const} = \frac{2a^2 N \Delta m_s}{q_0}.$$

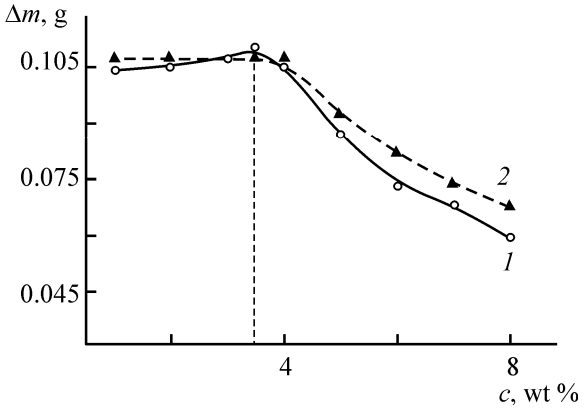

Fig. 2. Influence of the concentration of starch hydrogels c on the amount of starch Δm that passed into solution in the course of ultrasonic treatment (t = 20 s, f = 22 kHz). Curve: (*1*) experimental and (*2*) calculated.

The calculated dependence of Δm_{ac} on c is shown in Fig. 2 (curve *2*). For the same time of ultrasonic treatment, we obtained, using formula (11), the experimental values of Δm from the measured changes in the amount of the water-soluble fraction (Fig. 2, curve *1*). As can be seen, the calculated and experimental curves are in reasonable agreement, which confirms the correctness of our approaches. The data we obtained show that, with an increase in the starch concentration in the paster, the efficiency of its ultrasonic disintegration decreases. This is due to densification of grains, i.e., to an increase in the number of bonds cleaved per unit area of the newly formed surface.

Thus, we experimentally determined the required quantities and found relationships allowing prediction of the particle size in starch hydrogels upon their ultrasonic cleavage.

CONCLUSIONS

(1) The conventional energy of intermolecular interaction in swollen starch grains, characterizing their resistance to mechanical disintegration, was determined by an experimental and calculation procedure.

(2) A mathematical expression relating the expected particle size of the colloid phase and the water-soluble fraction content in starch hydrogels to parameters of their ultrasonic treatment was obtained.

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