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MECHANICAL PROPERTIES OF A COLLOIDAL BODY IN THE PROCESS OF ITS TRANSFORMATION INTO A CAPILLARY-POROUS ONE AS A RESULT OF DRYING

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The changes in the mechanical properties of a colloidal body in the process of its transformation into a capillary-porous one as a result of drying have been investigated by the example of casein. The rheological properties of casein were experimentally investigated by the method of mechanical Fourier spectroscopy. The mass loss and the shrinkage of this biopolymer were measured at different rates of conductive drying determined by the drying temperature. A macrokinetic model has been constructed. As the kinetic parameter, the relative mass loss was selected.

Introduction. The drying process is investigated mainly on the basis of consideration of the heat and mass transfer in the material being dried and the relation between the moisture content in the colloidal body and its transformation into a capillary-porous one as a result of the drying. Drying is a complex heat-engineering and technological process leading to nonreversible physical, mechanical, colloidal, and biotechnical changes in a material. Therefore, the study of the properties of a material subjected to drying is not only of scientific interest but also of practical importance [1–4].

A timely problem is the search for easily utilized decomposable materials of natural origin. It is known that biological polymers used in the production of different materials change their mechanical properties in the process of drying, with the result that a colloidal body is transformed into a capillary-porous one [5]. The study of the process of drying of such materials is of importance because this process represents the final stage of the technological treatment of a material and, therefore, determines the quality of the product obtained [6].

One of the most abundant biopolymers used widely in modern industry is casein, representing a protein with a molecular mass of about 20,000 kD. This protein has a complex chemical composition and possesses a set of mechanical and thermophysical properties manifesting themselves at all stages of its drying and, in the long run, determining the quality of the final product. A group of physical-mechanical properties of the indicated protein is formed by its structural-mechanical properties [7].

The drying of biological materials is widely covered in the literature; however, it is considered mainly from the technological-process standpoint [6], and the available data on the structural-mechanical (rheological) properties of these materials are insufficiently complete. It should be noted that the absence of reliable information on the rheological characteristics of biopolymers prevents their use for obtaining high-quality products that meet modern home and international standards.

It is the practice to dry materials at high temperatures for the purpose of increasing the output of final products. Such a treatment of materials increases the rate of evaporation of moisture from both the surface and the bulk of these materials, which leads to a nonreversible change in their physicochemical properties and determines the quality of the surface of the products obtained. The rate of moisture evaporation from a material is determined by the kinetics of the physicochemical transformations occurring in it in the process of its drying at a definite temperature T and for a definite time t_d. Large temperature and moisture gradients can cause a deformation of a material under the action of internal stresses as well as bulk and surface forces.

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Rapid removal of moisture from the free surface of a capillary-porous material leads to ordering of its structure and a decrease in the volume of the material, i.e., to its shrinkage and a nonreversible (plastic) deformation. Because of this, to optimize the drying of a material it is necessary to have a grasp of its stressed-strained state. For this it is necessary to know the structural-mechanical (rheological) properties of the material.

Let the material being dried be isotropic, and let it be considered a linear viscoelastic body. The viscoelastic properties of such a body completely determine its stressed-strained state in the process of one-dimensional drying. In this case, the stresses and deformations [8] are related as

$$2G_0(t)\,\varepsilon(t) = \sigma(t) + \int_{t_0}^{t} \Gamma(t, \tau)\,\sigma(\tau)\,d\tau\,. \qquad (1)$$

We will assume that moist casein is, from the mechanical and rheological standpoints, a linear hereditary-type medium with parameters defined by a functional relationship relating the temperature T and the humidity U to the instantaneous shear modulus of elasticity $G_0(U, T)$ and the relaxation effects represented by the relaxation spectrum $\Gamma(U, t)$ in Eq. (1). Unfortunately, not much is known about the changes arising in the mechanical properties of a colloidal body as a result of its transformation into a capillary-porous one in the process of drying because the method of determining these change has not yet been devised.

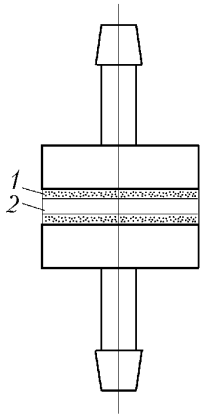
Note that the properties of the material being considered change with time. It is assumed that this change happens for a time that is larger than the time of an experiment. Since the material is subjected to nonreversible changes in the process of drying, Eq. (1) should involve an additional parameter reflecting the kinetics of change in its properties (including the mechanical ones), i.e., the parameters G_0 and Γ should also be functions of this kinetic parameter. It is difficult to experimentally determine the parameters of Eq. (1) in real time. Because of this, the structural-mechanical properties of a material subjected to drying are measured in the dynamic regime by the method of forced multifrequency vibrations (mechanical spectroscopy) [9].

Determination of the kinetics of the nonequilibrium processes occurring in a material in the process of its drying is a timely problem, the solution of which will make it possible to understand the physicochemical transformations to which the material is subjected as a result of the drying. Two different approaches to the solution of this problem — the kinetic approach and the macrokinetic one — can be used. If the kinetic approach is used, the stages of the drying process are investigated by direct physical methods. However, this approach is not always efficient from the standpoint of estimating the degree of the physicochemical transformation of a material subjected to drying. This is explained by the fact that these transformations involve many stages occurring both simultaneously and successively, and one and the same processes can result in obtaining products with absolutely different properties because the topology of the products obtained in one-type stages can be essentially different. The macrokinetic approach based on the determination of the time changes in any integral parameter characterizing all transformations of a material in the process of its drying is considered as most efficient for the present investigation.

Formulation of the Problem. The aim of the present work is 1) to investigate the change in the structural-mechanical properties of a colloidal body (by the example of casein) as a result of its transformation into a capillary-porous one in the process of drying, 2) to obtain experimental data on the rheological properties of this material and on the loss of moisture from it in the process of drying, 3) to determine the parameters of the elastic modulus and the relaxation spectrum of the material being investigated, and 4) to construct a model of a linear viscoelastic body.

Experimental Methods. *Method of mechanical Fourier spectroscopy.* Mechanical Fourier spectroscopy is based on the dynamic measurement of the parameters of rheological systems; in this case, a sample is acted upon by several frequencies at a time, and then the result of action of each frequency is analyzed. If the spectral compositions of the input and output signals are known, one can calculate the shear modulus G^* for each frequency ω_n. Consequently, the spectrum of the relaxation time is determined in the form of the relaxation kernel of an integral equation [9–13].

A material can be deformed by different laws; however, harmonic vibrations are used most frequently for this purpose, which is explained by the in-depth development of harmonic-analysis methods and the possibility to represent any periodic deformations in the form of a discrete or a continuous set of frequencies. However, the harmonic-vibration method is of limited usefulness: it requires that 1) the sample being investigated represents a linear system (small-



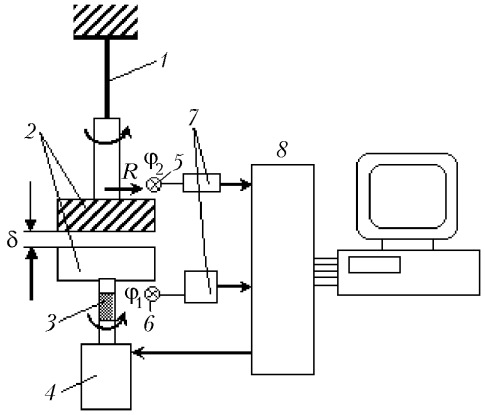


Fig. 1. Measuring unit: 1) porous metal; 2) sample.

Fig. 2. Diagram of a measuring device: 1) torsion; 2) measuring unit; 3) insulator; 4) VR-74 drive; 5, 6) angular movement sensors; 7) filters; 8) PCL-812 card.

amplitude deformations) and 2) this system be quasi-static. The initial experimental data are processed by known methods [8]. The method described was realized in the form of software allowing one to investigate the viscoelastic characteristics of a biopolymer in a real time.

Special measurement unit. To investigate the structural-mechanical properties of a material, it is necessary to load it so that uniform deformation of the material and moisture transfer in it are simultaneously provided. In accordance with these requirements, we have developed and fabricated a special measurement unit representing a disk–disk system (Fig. 1) with a working surface made from a porous material with a pore size of the order of 0.1 mm. The moisture from the body being investigated is transferred through a penetrable porous material of optimum thickness, which allows us to suggest that this process is uniform everywhere on the surface of the body. To provide such a transfer, disks of a porous metal 1 are pasted on the measuring surfaces (Fig. 1). The lower surface of the measuring unit is connected to the program-controlled drive of a vibrating-flow meter. A feature of this measuring device is that the rheological measurements are carried out in a thin layer of the material being investigated (of the order of 0.2 mm). This provides a uniform spatial distribution of the moisture content. Because of the geometry of the measurement unit, the rate of shear along the radius is variable. However, this configuration of the working unit provides uniform drying of sample 2 (Fig. 1) and makes it possible to investigate its mechanical properties. A sample should have a minimum thickness to provide a one-dimensional deformation (of the first rank), isothermal measurement conditions, and a uniform moisture transfer.

Device. The measurements were carried out on a VR-74 vibrating-flow meter (Moscow) designed for investigating anomalously viscous and viscoelastic liquids subjected to a continuous deformation with a constant rate and to a cyclic deformation with varying values of the frequency and amplitude. The device (Fig. 2) consists of an electromechanical drive, allowing it to be displaced by any definite law with a rotational velocity of 0–100 rpm, and is equipped with a torque-moment meter with fixation of the rotation axis by an air bearing with a sensitivity of 10^{-5} N·m and a measurement range of 10^{-5}–10^{-6} N·m. The device includes a controlled thermal chamber operating in the temperature range 20–170^{o}C and is equipped with a sensing element used for measuring the shrinkage of the material being investigated.

Automatized system of experimental investigations. A computer-aided system was used for interconnected automation of the processes of control of the experimental setup and the recording of effects as well as the collection, processing, and analysis of the data obtained [14]. The sensors of the angular movement of the upper and lower planes of the measuring unit were connected, through a high-pass filter (with a cut-off frequency of 18 Hz), to an A/D converter (PCL-812PG, Advantech, Taiwan) contained in an controlling computer. The output of the A/D converter is connected to the controlling drive of the vibrating-flow meter (Fig. 2). Thus, the whole measurement process is controlled by a computer. The sampling of measurement signals was carried out with the use of a specially developed software at 55-msec intervals. The deformation signal with a frequency allocation $\nu = 2^{n-1} = 1, 2, 4, 8, 16, 32$ and a fundamental frequency of 0.0088 Hz was determined by the formula

$$\varphi_1 = \sum_{n=1}^{6} A_n \cos(2^n \omega t) . \quad (2)$$

After the digital filtration, the data obtained were written in a file and the deformation and shear stress were calculated. The current deformation of the sample ε was calculated in accordance with the DIN 53018 standard [15] by the formula

$$\varepsilon = \varphi_1 R/\delta , \quad (3)$$

and the shear stress in the sample was determined from the equation

$$\sigma = \frac{3M}{2\pi R^3} , \quad M = C\varphi_2 . \quad (4)$$

In the process of measurement, the condition of small deformation was provided, i.e., $\varphi_2 << \varphi_1$.

Mass of a sample. The mass of a sample was determined accurate to 0.1 mg with the use of an analytical balance. The initial mass of the sample was equal to m_0 = 2–7 g. The shrinkage of the material in the process of drying was determined by a micrometer with an accuracy of 1 μm. The temperature was measured by a thermometer with an accuracy of 0.1°C. The range of change in the drying temperature T = 20–80°C satisfied the processing conditions.

Material under study. Casein was used as the experimental material. The casein concentrate was diluted with water to the required concentration. Then its aqueous solution was boiled down at a temperature of 20°C. The mass of the sample in the process of drying was determined by weighing.

Discussion of Results. *Macrokinetics.* Drying is a nonreversible multistage kinetic process, in the analysis of which it is difficult to separately consider the contributions of its individual stages as well as the temperature and humidity fields. Therefore, it would be reasonable to introduce the dimensionless integral parameter β characterizing the degree of humidity transfer from the material being investigated. This parameter is related, on the one hand, to the moisture content U in the material, and on the other to its mechanical properties. We think that the mass loss of the material being dried can be used as its main macrokinetic parameter.

Thus, the change in the mechanical properties of a material in the process of drying can be related to the elastic modulus $G_0(\beta)$ and the relaxation spectrum $\Gamma(\beta, \tau)$ of this material. This provides a means for solving two problems: on the kinetics of drying and on the stressed-strained state of the material in the process of drying, which makes it possible to determine the optimum time of drying for which the quality of the material is not adversely affected.

The viscoelastic properties and characteristics of a material are dependent on such of its parameters as the temperature T, the time of drying t_d, the moisture content U, the relaxation time τ, and the running time t. Because of this, we simultaneously investigated the mechanical properties of the material being studied and the kinetics of its transformation from the colloidal into the capillary-porous state in the process of drying. For the purpose of investigating the kinetics of drying of the material and determining its temperature dependence it is customary to experimentally measure the moisture content U in this material, which is a complex problem. In practice, it is easier to measure and use the dimensionless parameter of the relative mass loss

$$\beta = (m_0 - m_f)/(m_0 - m_d) = \Delta m/m_m . \quad (5)$$

The experimentally obtained time dependence of the mass loss of casein in the process of its drying is shown in Fig. 3.

The main kinetic problem is reduced to determination of the law of change in the degree of transformation of the material being dried with time. The behavior of β as a function of T is determined by the phenomenological equation of the drying kinetics

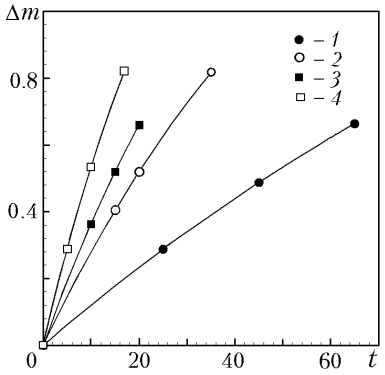


Fig. 3. Time dependence of the mass loss of a casein sample Δm in the process of drying (the points represent an experiment and the curves represent the forcing of data to fit Eq. (6)): T = 20 (1), 35 (2), 40 (3), and 45°C (4). Δm, g; t, min.

$$\dot{\beta} = K_0 \exp(E/RT) f(\beta) . \tag{6}$$

All actual drying processes can be described using the macrokinetic function $f(\beta)$. In accordance with Eq. (6), the rate of mass loss of the material in the process of its drying can be represented as the function of separated variables — the temperature T and the dimensionless mass loss β. In this case, the constants of the macrokinetic function $f(\beta)$ are independent of the temperature, and the activation energy of the physicochemical process is independent of the parameter β. The macrokinetic function of the drying process being considered can be defined by the following differential equation

$$\dot{\beta} = K(T)(1 - \beta) . \tag{7}$$

This equation defines the main parameters of the drying process and allows one to determine their temperature and concentration dependences. The temperature dependence (Fig. 3) obeys the Arrhenius law with an activation energy of 85 kJ/(K·mole).

Rheology. The law of transformation of a colloidal material into a capillary-porous one can be determined by the change in the elastic modulus of this material, reflecting the process of its drying in the integral form [5]. The deformation amplitude is measured in the linear region where the relaxation characteristics of the material remain unchanged when the deformation amplitude is varied. An experiment gives, at each instant of time, 12 values of the real components G' and G'' of the complex elastic modulus at a shift G^* [15].

It is known [9] that the viscoelastic properties of a material are characterized most completely by its relaxation spectrum $H(\omega)$ that is related, by a frequency dependence, to the dynamic modulus of elasticity $G^*(\omega)$ by the following relation representing an analog of Eq. (1):

$$G^* = G_0 + G_1 \int_{-\infty}^{\infty} \frac{i\omega\theta}{1 + i\omega\theta} H(\theta)\, d(\ln\theta) . \tag{8}$$

The calculation of $H(\theta)$ by the measured dependence $G^*(\omega)$ is appropriate and justified in the case where the frequency range is fairly wide. In our case, it would be reasonable to consider the relaxation characteristics of a viscoelastic body with a limited number of constants. The results of our measurements show that the simplest model of a linear viscoelastic body with a single relaxation time can be considered as this body. In this case, $G^*(\omega)$ is defined as [8]

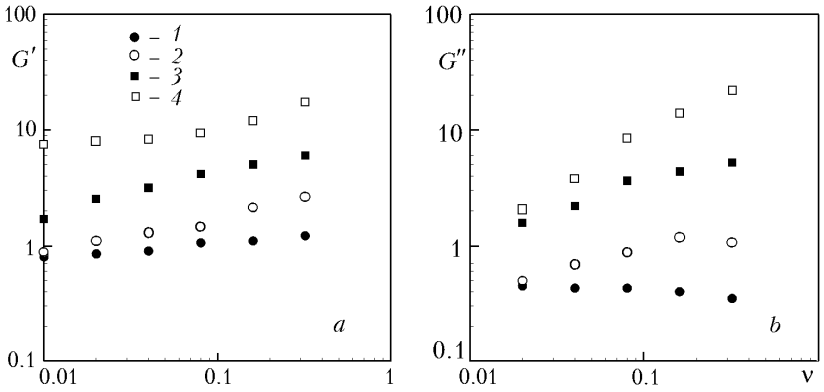


Fig. 4. Dependence of the dynamic modulus of elasticity (a) and the dynamic modulus of losses (b) on the frequency and time of the drying: t = 0 (1), 25 (2), 45 (3), and 65 min (4). G', G'', kPa; ν, Hz.

$$G^* = G_0 + G_1 \frac{i\omega\tau}{1 + i\omega\tau}. \tag{9}$$

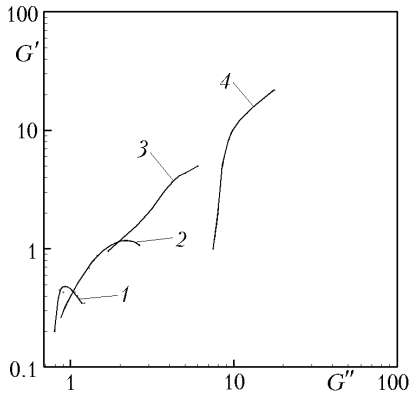
Equation (9) contains three constants: the instantaneous modulus of elasticity G_0, the characteristic time of relaxation τ, and the modulus of relaxation G_1, determined with the use of 12 measured quantities in the form of a pair of quantities (G^*, ω) at each instant of time. Here, of importance is that fact that the relaxation characteristics introduced are related to different physical mechanisms. The quantity G_0 reflects the existence of a three-dimensional net of bonds of aggregates forming the colloidal body, and the quantities G_1 and τ determine the relaxation caused by the flexibility of the aggregates and limited by their interaction and the net of temporal (fluctuation) bonds.

The results of measurements of $G^*(\omega)$ at a temperature of 25°C are presented in Fig. 4. It should be noted that the dependences shown in this figure have different forms at different times of drying. This effect manifests itself most markedly for the modulus of G'' because the positions of its maxima on the time axis are very different. In the most general sense, the measurement results obtained can be considered as evidence that the relaxation properties of the material being investigated contribute differently to its viscoelastic characteristics [14].

The results of measurements can be conveniently represented in the form of a diagram (Fig. 5) of the dependence $G'' = f(G')$ constructed for different times of structurization of the material being dried, in which the frequency of measurements is not considered as a parameter for the simplest model defined by expression (9). This dependence represents, in coordinates G'–G'', a semicircle with a radius $G_1/2$, the center of which is at a distance of $(G_1/2 + G_0)$ from the origin of coordinates. Thus, if a semicircle is constructed by six measurement points, two constants of model (9) are obtained, namely, the constants G_1 and G_0. The relaxation time is calculated for definite G_1 and G_0. The deformation of such a diagram with time is shown in Fig. 6. As is seen from this figure, the experimental points are adequately represented by the semicircles. Of interest is the time behavior of the indicated diagram. Until a definite characteristic instant of time, the semicircles move approximately along one and the same line and, in doing so, change their radius; in this case, the system being investigated is defined by the model of a standard viscoelastic body and represents a viscoelastic liquid with a varying viscosity (G_1 is a slightly changing variable; only the relaxation time changes, i.e., the flexibility of the aggregates increases).

At any instant of time, the parameter G_1 sharply increases, i.e., the mechanism of structure formation changes — the colloidal body is transformed into a capillary-porous one. Accordingly, the physical meaning of the constants of the models (Fig. 6), defined by expression (9), changes, i.e., the viscoelastic fluid is transformed into the viscoelastic body. It is seen from Fig. 6 that the parameters of the material being dried are varied in a fairly narrow time interval (for 10 min) during the drying, lasting for 65 min.

The results of our investigations allow the conclusion that expression (8) can be used for description of the change in the mechanical properties of a viscoelastic body in the process of its drying. In this case, the relation between the stress and deformation of this body has the form



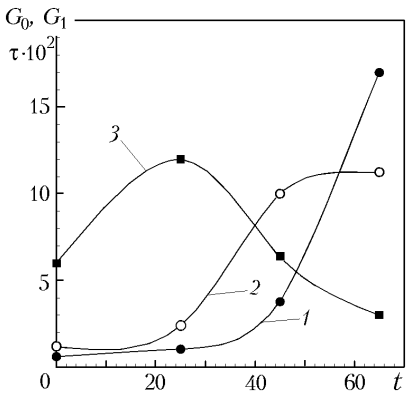


Fig. 5. Deformation of the Cole-Cole diagram in the process of drying. Designations 1–4 are identical to those in Fig. 4. G', G'', kPa.

Fig. 6. Change in the parameters of model (9) in the process of drying: 1) G_0; 2) G_1; 3) τ.

$$\dot{\beta} = K(T)(1-\beta); \quad \sigma(\beta, \tau(\beta)) = \frac{G_0(\beta) G_1(\beta)}{G_0(\beta) + G_1(\beta)} \varepsilon_0 \left[1 + \frac{G_0(\beta)}{G_1(\beta)} \exp\left(-\frac{t}{\tau(\beta)}\right)\right], \quad \beta(t=0) = 0. \tag{10}$$

Conclusions. The structural-mechanical (rheological) properties of a colloidal body as well as its mass loss and shrinkage as a result of the transformation into the capillary-porous body in the process of drying have been investigated by the example of casein. The rate of the conductive drying was changed depending on the temperature. The properties of the material being dried were determined by the method of mechanical Fourier spectroscopy that allows one to obtain information on the parameters of the instantaneous modulus of elasticity at a shift $G_0(\beta)$ and the relaxation kernel $\Gamma(\beta, \tau)$. The simplest model of a linear viscoelastic body with a definite relaxation time and variable parameters determined by the kinetics of the drying has been constructed. It was established that the kinetics of drying can be described by the first-order macrokinetic equation.

NOTATION

A_n, amplitude, m; C, rigidity of a torsion, N·m; E, activation energy of the transformation of a colloidal body into the capillary-porous one, J/mole; f, function of variables; G', real component of the complex modulus of elasticity, Pa; G'', imaginary component of the complex modulus of elasticity, Pa; G^*, complex modulus of elasticity, Pa; G_0, instantaneous modulus of elasticity, Pa; G_1, relaxing modulus of elasticity, Pa; H, relaxation spectrum; i, imaginary unit; K, function of variables; M, torque moment, N·m; m_0, initial mass of a sample, g; m_m, mass of the total moisture found in the sample in the period from the beginning of drying to its complete dehumidification, g; m_f, mass of the sample at the end of the drying, g; m_d, mass of the completely dehumidificated sample, g; Δm, mass of the moisture evaporated during the experiment, g; R, radius, m; T, temperature, °C; t, time, sec; t_d, time of drying, sec; U, average moisture content, kg/kg; β, dimensionless parameter of the relative moisture loss; Γ, relaxation spectrum; δ, clearance, m; ε, deformation of the sample; ε_0, definite deformation of the sample; η, dynamic viscosity, Pa·sec; θ, integration parameter; ν, frequency, Hz; σ, shear stress, Pa; τ, relaxation time of the system, sec; φ_1, rotation angle of the movable (lower) part of the measuring unit, deg; φ_2, rotation angle of the upper part of the measuring unit, deg; ω, frequency, Hz. Subscripts: 0, initial state; *, complex quantity; n, number of a frequency; m, moist; d, dry; f, final; point above a symbol, time derivative.

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