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# Dynamic surface properties of oat protein dispersions

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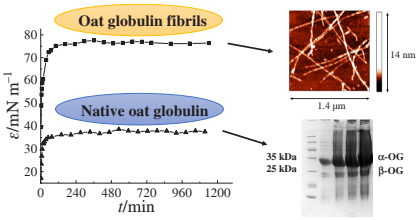
**Dynamic surface properties of the dispersions of a plant protein, oat globulin, were determined in a broad concentration range. The dilational dynamic surface elasticity of the dispersions exceeded significantly the values for native protein solutions indicating that fibrils can effectively stabilize multiphase disperse systems; thus, they can find various applications in the production of new materials.**




*Keywords*: plant protein, oat globulin, fibrils, surface rheology, surface tension, dilational dynamic surface elasticity.

The replacement of animal-based proteins by cheaper, healthier, and more ecologically friendly plant proteins in various technical applications is currently discussed in the literature.[1–3] The problem is not simple because the functionality of plant proteins is usually inferior to that of animal proteins.[1] A possible solution consists in the use of protein fibrils instead of native proteins.[4–6] The surface properties of the dispersions of protein fibrils can differ from those of native protein solutions, and they are important for the formation of thin films and multiphase systems including biodegradable and biocompatible materials.[2,3] At the same time, information about the surface properties of fibril dispersions is scarce. Recently, dilational surface rheology, ellipsometry, and atomic force microscopy were applied to study adsorption layer formation in the dispersions of fibrils of animal-based proteins.[7] In this work, we applied this approach to the dispersions of fibrils of a plant protein, oat globulin (OG). To the best of our knowledge, only the surface tension of the dispersions of the fibrils of this protein was determined previously.[4]

Oat globulin is the main storage protein of oats, and the OG fibril behavior in aqueous bulk phases has attracted attention recently due to possible use in water purification, sensors, and patterned electrodes.[6,8,9]

Oat globulin was prepared from ground and defatted oat groats using a procedure described by Zhou *et al.*[8] (The SDS-PAGE image of the protein is given in Figure S1 of the Online Supplementary Materials.) Freeze-dried OG powder was dissolved in triply distilled water and the solution pH was adjusted to 2. After that, the solution was incubated at 90 °C with stirring for 18 h to produce mature OG fibrils. Figure 1 shows the atomic force microscopy (AFM) image of the fibrils.

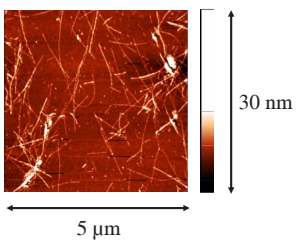



**Figure 1** AFM image of OG fibrils.

Surface tension was measured by the Wilhelmy plate method, and dilational dynamic surface elasticity was determined by the oscillating barrier method as described elsewhere.[7,10] The micromorphology of the fibrill layers and their transfer to mica and the measurement of ellipsometric angles were performed.[†]

Oat globulin was characterized by a significant surface activity, and it decreased the surface tension down to 54 mN m$^{-1}$ at a concentration of 0.1 g dm$^{-3}$ (Figure S2).

At the same time, the real part of the dynamic surface elasticity reached about 40 mN m$^{-1}$ (Figure S3), a little lower than the values for the solutions of most animal proteins.[12] The real part of the dynamic surface elasticity significantly exceeded the imaginary part for all the systems in this study and only the former one is shown below. All the kinetic dependences of the dynamic surface elasticity of protein solutions were monotonic, indicating a relatively rigid tertiary structure of the protein.[12]

The surface properties of the dispersions of OG fibrils changed faster with the surface age than the surface properties of native OG solutions. As an example, Figure 2 shows the kinetic dependences of surface tension and dynamic surface elasticity at a protein concentration of 0.005 g dm$^{-3}$. However, qualitatively similar results with faster changes of the surface properties of fibril dispersions than those in native protein solutions were observed for all of the studied systems in the concentration range of 0.001–0.1 g dm$^{-3}$. Fast changes of the surface properties of fibril dispersions were observed in animal-based proteins and explained by the fast adsorption of polypeptide impurities formed in the course of fibril formation at elevated temperatures.[7,13] The strong influence of polypeptides (protein fragments) on the kinetics of adsorption was also confirmed for dispersions of fibrils of a plant protein, soy protein.[14] Small peptides with a relatively high diffusion coefficient significantly reduced surface tension at the initial adsorption steps.

[†] The micromorphology of the fibril layers was determined by AFM using an NTEGRA Spectra instrument (NT-MDT, Russia) in a semicontact mode. The Langmuir–Schaeffer method was applied to transfer a fibril layer from the liquid surface onto a mica plate.[7] The ellipsometric angles of the solutions were measured with a Multiskop null-ellipsometer (Optrel GBR, Germany) at a wavelength of 632.8 nm and at a fixed compensator position (±45°) using a 2-zone averaging nulling scheme.[11]

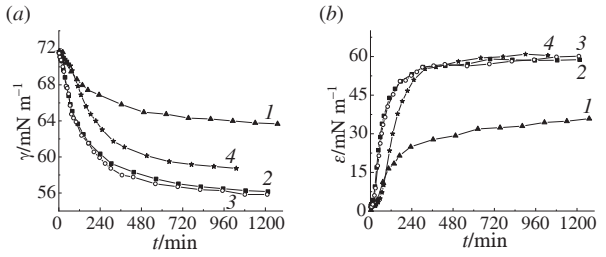



**Figure 2** Kinetic dependences of (*a*) the surface tension and (*b*) dynamic surface elasticity of (*1*) native OG solutions and dispersions of (*2*) unpurified fibrils and fibrils purified by (*3*) short centrifugation and (*4*) long centrifugation. The protein concentration was 0.005 mg ml$^{-1}$.

To test the influence of impurities, the OG fibril dispersions were centrifuged at 15,500×*g*. After that, the supernatant was carefully removed, and the precipitate was used for the preparation of aqueous fibril dispersions at pH 3. The total protein concentration after centrifugation was determined by thermogravimetry. The purification led to slower changes in the surface properties (Figure 2). The rate of change with a long centrifugation for approximately 60 min was lower than that with a short centrifugation for 10 min due to a stronger influence of the impurities in the latter case.

Although the purification procedure influenced the kinetic dependences of the surface tension and the dynamic surface elasticity, it had almost no influence on the dependence of the surface elasticity on surface pressure (Figure 3). For dispersions of amyloid fibrils of β-lactoglobulin (BLG) and lysozyme, the dependences of surface elasticity on surface pressure coincided with the corresponding results for solutions of native proteins, indicating that the surface properties were determined by polypeptides of relatively low molecular weights even in purified dispersions.[7] This was not the case for the system under investigation. The dynamic surface elasticity of OG fibril dispersions exceeded the value for OG solution at the same surface pressure (Figure 3). Moreover, this was true even for unpurified dispersions. Thus, the surface properties of the dispersions were determined by a fibril network in the surface layer. The purification decreased the concentration of low-molecular-weight polypeptides and the adsorption rate but changed the adsorption layer structure only slightly.

The dynamic surface elasticity of OG fibril dispersions, like the surface elasticity of native protein solutions, increased monotonically with the surface pressure, confirming the adsorption of relatively rigid particles, fibrils, and protein globules and the lack of flexible chains in the surface layer. This behavior is opposite to that of spread layers of the plant protein cupin-1.1, when partly unfolded protein molecules and a loose corona of protein particles at the interface led to local maxima and minima of the dynamic surface elasticity as a consequence of the formation of a distal region of the adsorption layer at an increase of the surface pressure.[15]

The adsorption of OG fibrils decreased the surface tension stronger than the adsorption of protein molecules (Figures 2 and 3), down to 59 mN m$^{-1}$ at a concentration of 0.005 g dm$^{-3}$. At this concentration, the surface tension of native OG solutions decreased only to approximately 65 mN m$^{-1}$. The surface elasticity of the dispersions reached ~55 mN m$^{-1}$ while it approached only 35 mN m$^{-1}$ in the protein solutions. An increase in the fibril concentration led to ~75 mN m$^{-1}$ at a concentration of 0.1 g dm$^{-3}$. Note that the dynamic surface elasticity is the main parameter determining the stability of emulsions and foams.[16,17]

The results indicated the higher surface activity of OG fibrils and a stronger adsorption layer in the dispersions than those in native OG solutions presumably due to a higher local concentration of amino acid residues at the interface in the former case.

The ellipsometric results confirmed this assumption (Figure 4). The ellipsometric angle Δ is approximately proportional to the adsorbed amount,[18,19] and the values for OG fibril dispersions exceeded noticeably data for the native protein solutions at the approach to equilibrium indicating the higher surface concentration in the former case. The difference between the results for dispersions of purified and unpurified fibrils was close to the error limits, although Δ was a little higher for unpurified fibrils. This means that the fibril adsorption occurred even in unpurified dispersions influencing their surface properties. At the same time, purification decelerated changes in the ellipsometric angle confirming a decrease in the concentration of low-molecular-weight polypeptides, in agreement with the results on surface tension and dynamic surface elasticity (Figure 2).

An increase in solution ionic strength by the addition of NaCl increased slightly the angle Δ close to equilibrium and, hence, the adsorbed equilibrium amount (see Figure 4). This was presumably due to a decrease in the electrostatic repulsion between fibrils in the surface layer and the formation of a more compact layer structure. Another effect of the increase in the solution ionic strength was an acceleration of changes in the surface tension and dynamic surface elasticity due to a decrease in the electrostatic adsorption barrier (Figure S3). However, this effect was much stronger in solutions of native OG indicating a stronger adsorption barrier in this case. Presumably, there was an excess of charges of the same sign at the surface of OG, globules and possible amorphous aggregates leading to a relatively high surface potential, while the excess charge at the surface of fibril aggregates was compensated to a higher extent by oppositely charged groups.

The transferring of an adsorption layer of fibril dispersions from the liquid surface onto the surface of mica by the Langmuir–Schaeffer technique and the application of AFM showed that the layer was not microscopically homogeneous, and it contained some clusters of fibrils (Figure 5). At the same time, the smooth kinetic dependences of ellipsometric angles did not indicate the formation of macroscopic aggregates in the surface layer.

The results obtained for fibril dispersions of the plant protein OG showed similarities with the surface properties of the fibril dispersions of most animal proteins. The formation of low-molecular-weight polypeptides and high surface activity in the

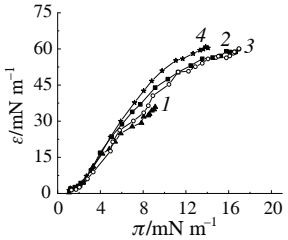



**Figure 3** Dependences of the dynamic surface elasticity on surface pressure of (*1*) native OG solutions and dispersions of (*2*) unpurified fibrils and fibrils purified by (*3*) short centrifugation and (*4*) long centrifugation. The protein concentration was 0.005 mg ml$^{-1}$.

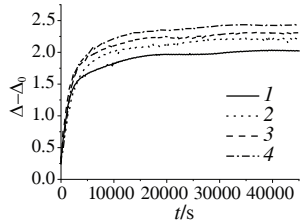



**Figure 4** Kinetic dependences of the ellipsometric angle Δ of (*1*) native OG solutions and dispersions of (*2*) fibrils purified by long centrifugation, (*3*) unpurified fibrils, and (*4*) fibrils purified by long centrifugation with 0.1 M NaCl. The protein concentration was 0.005 mg ml$^{-1}$.

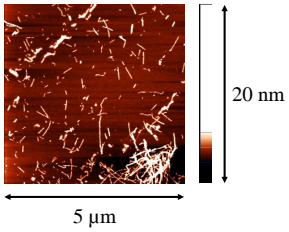



**Figure 5** AFM image of the adsorption layer of purified OG fibrils after long centrifugation transferred from the surface of an aqueous 0.1 M NaCl solution. The fibril concentration was 0.005 mg ml$^{-1}$.

course of fibril preparation resulted in the contamination of the system and careful purification did not give a possibility to get rid of the impurities. At the same time, unlike the fibrils of BLG and lysozyme, the surface activity of OG fibrils was significantly higher than that of native protein molecules, and the dynamic surface elasticity exceeded the values of native protein solutions even in unpurified OG dispersions. The surface properties were strongly influenced by fibril adsorption; therefore, the OG fibrils can find various applications related to the formation of stable emulsions and foams.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7597.

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