Influence of high pressure treatment on the rheological characteristics of fish paste

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Abstract. The paper presents a comparative analysis of the results of experimental studies of the rheological characteristics of the fish paste prepared by the traditional method and the paste obtained using high pressure treatment at room temperature. The viscosity and shear stress were studied, which characterize the forming ability and strength of the structure. It is shown that pressure treatment can be used as an alternative way to prepare fish paste.

1. Introduction
In order to assess the technological and organoleptic properties of a fish paste obtained using high pressure (up to 600 MPa) [1], we studied its structural and mechanical properties. Structural and mechanical properties of the paste depend on the volume ratio of the dispersed phase and the dispersion medium, the nature and strength of the bonds between the medium and the dispersed particles, and the nature and strength of the bonds between the particles. In accordance with the classification of P.A. Rebinder, they exhibit the properties of coagulation, condensation and crystallization structures [2]. Structural and mechanical characteristics reflect the state of proteins and their water-binding ability, and can be used to assess the impact of technological treatment on the quality of the finished product.

2. Problem statement
Structural and mechanical properties of the products, depending on the structure of the tissue, also characterize the consistency of the product. Most researchers consider the consistency (tenderness) of the product as the organoleptic equivalent of the product’s resistance to deforming and destructive forces. But it should be noted that the sensory concept of tenderness of a product is wider and includes a complex of sensations that reflect such properties of the tissue as fiber strength, softness, density, juiciness.

3. Materials and methods
As basic rheological properties, we studied viscosity, which is a generalized characteristic of the
complex structure of pastes, and shear stress, which characterizes the shape-forming (shape-holding) ability and stability of the structure.

The objects of rheological research were 3 samples:
- sample No. 1 - raw paste mince;
- sample No. 2 - paste obtained in the classical way;
- sample No. 3 - paste treated with a pressure of 570 MPa for 25 minutes.

To visualize the flow curves, a RHEOTEST RN4.1 rotational viscometer (Germany) was used, which provides high accuracy in obtaining absolute values of indicators with automatic continuous recording of the obtained data in a data file. In accordance with the recommendations, a cylinder-to-cylinder measuring system with an N1 type rotor was chosen for research, since the test samples have a sufficiently high viscosity.

To obtain reliable flow curves, the experiment was repeated three times. The temperature 22±0.1 °C was uniform throughout the sample volume and was maintained by thermostat control; the samples did not undergo chemical transformations and had a uniform consistency.

We obtained the averaged values of the effective viscosity of the paste samples $\eta_{ef}(D)$, shear stress $\theta(D)$ depending on the shear rate $D$ (table 1).

### Table 1. The results of experimental studies.

| Shear stress, Pa | Effective viscosity, Pa·s | Shear rate, s⁻¹ | Shear stress, Pa | Effective viscosity, Pa·s | Shear rate, s⁻¹ | Shear stress, Pa | Effective viscosity, Pa·s | Shear rate, s⁻¹ |
|-----------------|--------------------------|-----------------|-----------------|--------------------------|-----------------|-----------------|--------------------------|-----------------|
| 4.632           | 410                      | 0.024           | 72.4            | 2790                    | 0.08            | 52.7            | 2410                    | 0.08            |
| 114             | 203                      | 2.59            | 810             | 2069                    | 0.09            | 357.9           | 1634                    | 0.09            |
| 186             | 7.211                    | 25.17           | 1630            | 669                     | 35.8            | 507             | 245                     | 35.8            |
| 238             | 5.368                    | 44.83           | 2270            | 57.12                   | 65.7            | 629.4           | 27.6                     | 65.7            |
| 258             | 3.568                    | 64.11           | 2596            | 36.54                   | 88.4            | 753             | 25.8                     | 88.4            |
| 264             | 2.357                    | 84.35           | 2770            | 32.15                   | 108.6           | 853.6           | 23.4                     | 108.6           |
| 286             | 1.385                    | 108.4           | 2940            | 30.14                   | 124.7           | 957.1           | 18.6                     | 124.7           |
| 315             | 1.014                    | 135.2           | 3080            | 28.62                   | 142.6           | 1060            | 17.8                     | 142.6           |
| 323             | 0.988                    | 153.3           | 3110            | 20.16                   | 167.5           | 1180            | 15.5                     | 167.5           |
| 335             | 0.752                    | 174.8           | 3210            | 19.58                   | 197.8           | 1250            | 13.5                     | 197.8           |
| 362             | 0.566                    | 195.5           | 3310            | 18.24                   | 210.7           | 1280            | 10.72                    | 210.7           |
| 384             | 0.496                    | 215.4           | 3350            | 16.54                   | 218.8           | 1320            | 9.83                     | 218.8           |
| 384             | 0.482                    | 218.6           | 3350            | 14.18                   | 226.7           | 1320            | 8.54                     | 226.7           |

4. Analysis of indicators
Figure 1 shows the flow curves built according to the experimental data.
The flow curves demonstrate that each value of the shear rate corresponds to a certain equilibrium state of the product structure. Raw paste mince, as well as pastes obtained as a result of heat treatment (classical technique) and high pressure treatment, are non-Newtonian solid systems with pronounced pseudoplasticity.

With an increase in the shear rate, the viscosity decreases and stabilizes upon transition to the region of the destroyed structure. When the shear rate is exceeded 65 s$^{-1}$, the rate of change in viscosity values decreases significantly. Fluctuations of shear stress value depending on the state of the samples are significant.

From the presented graphs it can be seen that the quantitative values of the rheological characteristics of the samples vary significantly. The rheological characteristics of a fish paste prepared using classical technology show an increase in values, associated primarily with a change in the state of protein molecules stabilizing a paste emulsion. In addition to thermal denaturation, the cooking process is accompanied by a number of additional physicochemical changes: shrinkage and disaggregation of collagen; a change in the structural and mechanical properties, organoleptic characteristics; a change in the state and properties of fats, inactivation of vegetative forms of microorganisms.

It is known that when heated, proteins undergo complex physicochemical changes, primarily denaturation and coagulation, on the depth of which the structure and quality of the finished product depend. These processes are accompanied by the expansion of globules and the release of free side groups of amino acids, and therefore, there is the possibility of the formation of intermolecular bonds, aggregation of particles and their deposition leading to a decrease in the solubility of proteins. The restructuring of the protein molecule during denaturation weakens the hydrophilic and enhances the hydrophobic properties, therefore, the protective effect of the hydration layers near the polar groups decreases, which leads to an increase in the strength properties of the paste. The bulk of the protein

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**Figure 1.** Flow curves.
coagulates between 55 °C and 65 °C, and most intensively at pH = 5.5. At 80 °C, all proteins are deposited. As a result of thermal denaturation, the solubility, degree of hydration, the level of emulsifying ability of proteins, the nature of bonds, the ratio of hydrophilic and hydrophobic groups change, a fixed three-dimensional protein structured framework with pronounced elastic properties is formed [3]. The depth of these changes depends on the temperature of the product and the time of treatment.

When the product is exposed to high temperatures for a short time, the denaturation of the protein system occurs quickly, as a result of which the resulting matrix can cause sharp shrinkage and displacement of moisture, and the finished product will have a low juiciness and yield. Soft heat treatment modes (heating temperature 75-80 °C) provide a higher yield of finished products, better juiciness and tenderness of products, but cause a prolonged heat treatment process.

Coagulation changes in proteins upon heating lead to a qualitative change in the structure of the paste, which largely loses the viscoplastic properties of raw mince, and it begins to flow like a solid body. The paste becomes denser and harder.

In the case of treatment with high pressure, the values of the rheological parameters also increase in comparison with the raw material for the paste, but to a much lesser extent than during heat treatment. The increase in viscosity and strength properties is also associated with the denaturation of soluble albumin contained in raw mince. The denaturation changes that occur depend on the magnitude of the pressure. It is known that at pressures from low to medium (up to 150 MPa), hydrogen bonds responsible for the stabilization of the helical structure of peptides are strengthened.

In this case, the onset of denaturation does not occur. High pressure disrupts hydrophobic interactions, leading to a decrease in system volume. We used pressures of 570 MPa, at which irreversible denaturation of proteins is observed, which is directly proportional to the magnitude of the pressure and the duration of its exposure. This phenomenon can be explained by the violation of intermolecular ionic bonds of protein molecules under the influence of pressure. When the peptide chain is unwound, a large number of non-polar bonds are formed that are accessible to water. As the residues of the ionized groups interact with water dipoles, intermolecular bonds are reduced, causing a decrease in the volume of the system. As in the case of heat treatment, coagulation changes in proteins lead to a transition from a viscoplastic type of flow to a pseudoplastic flow.

The results of experimental studies showed that the samples have a stable structure, the destruction of which begins only when a certain shear stress is reached.

The paste treated with high pressure was more homogeneous, less viscous, strong and solid, which is consistent with the organoleptic examination, which noted the great tenderness, density, and juiciness of such a paste.

5. Analysis based on a software block
To determine the nature of the flow structure of the samples under study using the FindGraph software, empirical dependencies are used that describe the obtained experimental flow curves.

After analyzing the laws that take into account that the samples under study have a yield point, viscosity is a function of shear rate, the yield curve does not start from the origin, we determined that the shear stress dependence on the shear rate gradient is described with a high degree of accuracy by the Casson equation [4]:

\[
\frac{1}{\theta^*} = \frac{1}{\theta_0^n} + \left(\eta \cdot D\right)^n, \tag{1}
\]

where \(\theta_0\) (Pa) - ultimate shear stress at which the flow of the sample begins;

\(D\) (1/s) - shear rate gradient;

\(\eta\) (Pa·s) - viscosity;

\(n\) - a measure of the curvature degree of the flow curve.
The dependence of the viscosity of the samples on the shear rate gradient is described by exponential laws.

Table 2 shows the equations describing the flow curves of the studied samples obtained by processing the experimental data.

**Table 2. Equations for the description of the flow curves of the studied samples.**

| Rheological characteristic | Sample type | Laws of flow | Multiple $R^2$ |
|---------------------------|-------------|--------------|----------------|
| Shear stress              | Sample No.1 | $\theta^{\frac{1}{299}} = 947.9^{\frac{1}{299}} + (1.24D)^{\frac{1}{299}}$ | 0.912 |
|                           | Sample No.2 | $\theta^{\frac{1}{299}} = 990^{\frac{1}{299}} + (11.9D)^{\frac{1}{299}}$ | 0.85  |
|                           | Sample No.3 | $\theta^{\frac{1}{299}} = 378.29^{\frac{1}{299}} + (8.468D)^{\frac{1}{299}}$ | 0.96  |
| Viscosity                 | Sample No.1 | $\eta = 412.638 e^{-0.274D}$ | 0.999 |
|                           | Sample No.2 | $\eta = 2442.2 e^{-0.04D}$ | 0.972 |
|                           | Sample No.3 | $\eta = 4506 e^{-0.10D}$ | 0.967 |

Figures 2 - 7 show the base and response surfaces of the dependences of the structural and mechanical properties and the shear rate gradient for the samples under study. Table 3 shows the equations describing the dependence of structural and mechanical properties and shear rate.

Modeling of component structures allows visualizing the basic and fragmented sections of the model with the elements of the function extremum [5,6].

![Figure 2](image)

**Figure 2.** The base surface of the dependence of structural and mechanical properties and the shear rate gradient for raw paste mince.
Figure 3. The response surface of the dependence of structural and mechanical properties and the shear rate gradient for raw paste mince.

Figure 4. The base surface of the dependence of structural and mechanical properties and the shear rate gradient for the paste sample obtained in the classical way.
Figure 5. The response surface of the dependence of structural and mechanical properties and shear rate gradient for a paste sample obtained in the classical way.

Figure 6. The base surface of the dependence of structural and mechanical properties and the shear rate gradient for a paste sample treated for 5 minutes with a pressure of 570 MPa.
Figure 7. The response surface of the dependence of structural and mechanical properties and shear rate gradient for a paste sample treated for 5 minutes with a pressure of 570 MPa.

\[
\theta = a + bD + cD^2 + d\eta_{ef},
\]

where \( a, b, c, d \) - equation constants.

Table 3. Equations for describing the dependence of structural and mechanical properties and shear rate.

| Sample type | Laws of flow | Multiple \( R^2 \) |
|-------------|--------------|---------------------|
| Sample No.1 | \( \theta = 187.5 + 0.959D - 0.0003D^2 - 0.432\eta_{ef} \) | 0.999 |
| Sample No.2 | \( \theta = 1619 + 13.3D - 0.025D^2 + 0.5\eta_{ef} \) | 0.999 |
| Sample No.3 | \( \theta = 386.5 + 4.71D - 0.002D^2 - 0.1\eta_{ef} \) | 0.999 |

6. Conclusions

Thus, high pressure treatment can be used as an alternative way to prepare fish paste. Moreover, the obtained paste is characterized by greater uniformity, lower viscosity, strength, greater tenderness, density and juiciness compared to the paste obtained by classical technology, which is associated with the different course of denaturation processes during heat treatment and high pressure treatment.

References

[1] Sokolov S, Sevatorov N, Malich A 2018 Collection of works based on materials of scientific and practical conferences of teachers, graduate students and employees of FSBEI HE “KSMTU” (Federal Agency for Fisheries; Kerch State Marine Technological University) pp 201-208

[2] Nemtseva M, Phillipov D 2006 Rheological properties of colloidal systems: guidelines (Ivanovo) p 32
[3] Schukin E, Pertsev A, Amelina E 2007 Colloid chemistry (M.: Vysshaya shkola)
[4] Kosoy V 2005 Engineering rheology of biotechnological environments: textbook (SPb: GIORD) p 643 ISBN 5-901065-91-3
[5] Nyrkov A, Zhilenkov A, Sokolov S, Chernyi S 2018 Automation and Remote Control 79 1 pp 195-202
[6] Chernyi S, Zhilenkov A, Sokolov S, A Nyrkov 2017 Vibroengineering PROCEDIA 13 pp 261-265