Thermal structuring of fish gelatin

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Abstract. Currently, fish gelatin is of special interest on the market of biopolymers due to its safety, natural protein composition, high quality indicators and compliance with ethno-cultural peculiarities of nutrition. It has individual features, including reduced thermostability. Physical modification that occurs under the influence of temperature and has an impact on the equilibrium process of globular and fibrillar conformation transitions was carried out in order to improve the functional and technological properties of fish gelatin. The object of the study was fish gelatin obtained using innovative technology from scales of fish from the Volga-Caspian basin and commercial aquaculture facilities. Standard and original research methods were used in the study. Heat treatment was simulated depending on the temperature and duration of the process. Viscosity values variation of a 10% fish gelatin solution by 96.3% was caused by two factors. Influences caused by other factors are no more than 4 %. The possibility of structuring fish gelatin by high temperature treatment was determined. The rational mode of heat treatment is the temperature range from 125 to 130 °C. During the heat treatment at 135-140 °C, there is an increase in the duration of dissolution of fish gelatin and fragility of the plates along with a significant increase in the viscosity of solutions. Heat treatment of fish gelatin with residual moisture content of 10-16%, given the developed technological regimes and conditions, promotes the formation of a polymer network (cross-linking), improving the consumer properties, performance of fish gelatin, and its hydrolytic stability.

1. Introduction

Fish gelatin, which is a product of processing of fish collagen-containing raw materials, has recently been given a special place in the scientific and publicistic literature. Fish gelatin is an analogue of animal gelatin produced from bones and soft collagen-containing raw materials of cattle and pigs. In contrast to the traditional structural agent, fish gelatin is a safe ingredient and has no risk of contamination of the human body with agents of prion (infectious) diseases through the organs and tissues of ruminants and products of their processing. In addition, fish gelatin is more physiological to humans and is better absorbed by the human body. Compliance of fish gelatin with the trends of ethno-cultural features of production of products for various purposes allows it to compete with animal gelatin [1, 2].

Regulatory documents characterize the rheological properties of gelatin by the following physical and chemical quality parameters: melting point, strength of the gel formed (jelly), dynamic viscosity of the gelatin solution. Fish gelatin has individual features and is characterized by a lower melting point value of jelly on average by 4 °C, an increased value of the dynamic viscosity of fish gelatin...
solutions on average by 7 mPas compared with the regulated requirements for animal gelatin. Reduced thermostability is typical for fish collagen-containing gelatin and depends mainly on the amino acid composition. Rheological properties of gelatin are in direct dependence on the dynamic viscosity of the gelatin solution, i.e., the higher the value of the dynamic viscosity of the gelatin solution, the higher the rheological parameters and the higher its efficiency [3].

Literary sources [4, 5] show that the stabilizing properties of gelatin can be adjusted by modification, resulting in changes in the hydrophilic balance of gelatin macromolecules and their conformation state. Therefore, it is advisable to consider methods of its structuring in order to improve the functional and technological properties and performance of fish gelatin.

It is known that the so-called cross-linking of gelatin molecules is performed not only by treatment with chemical agents, but also by heat treatment. Modification of gelatin and changes in its structural elements resulting from heat treatment are physical modifications and represent an equilibrium process of globular and fibrillar conformation transitions. Both fibrillar and globular tertiary conformations are typical for gelatin [4, 6].

2. The purpose of the study
The most effective way to structure gelatin is to use chemical modifiers. Glutaraldehyde is a common and effective structuring agent. However, its main drawback is its toxicity, so there is a question of finding alternative methods of gelatin modification [7].

Thermal modification is a safer treatment method without the use of toxic chemical cross-linking agents. The issues of thermal structuring were considered by the researchers of the A.N. Bakulev National Medical Research Center of Cardiovascular Surgery under the Ministry of Health of Russia. They considered these issues on the example of film compositions based on animal gelatin produced from collagen-containing raw materials of cattle and pigs [8].

The issues of enhancing intermolecular interaction and stabilizing fish gelatin have been poorly studied. In connection with the foregoing, it was of interest to evaluate the possibility of structuring fish gelatin by heat treatment.

3. The object of the study
Fish gelatin derived from scales of fish from the Volga-Caspian basin and commercial aquaculture facilities using innovative technology was used as the object of the study.

4. Materials and methods
The experiments were conducted in the laboratories of the Astrakhan State Technical University with the use of analytical and drying equipment with the principle of convection.

The study of organoleptic and physicochemical indicators of fish gelatin quality was conducted using standard methods. Viscosity of fish gelatin solution was measured by instrumental method using capillary glass viscometer.

Processing of experimental data was carried out by methods of mathematical statistics, including standard programs and common algorithms using regression analysis and optimization via Microsoft Office 2010 application package with a 95% probability of output. In order to implement the orthogonal central composition plan of the two-factor experiment, we used statistical data processing via Statistica 10.0 software and recalculation of dimensionless coefficients into real values.

In order to evaluate the effectiveness of thermal modification of fish gelatin, we studied the dependence of the dynamic viscosity of a 10% of fish gelatin solution, which characterizes the rheological properties, on the temperature and duration of the heat treatment process. The viscosity of fish gelatin solutions was determined before and after the heat treatment.

Values of variable factors, their levels, intervals and limits of variation, as well as the plan of the experiment to model the viscosity of fish gelatin solution are presented in Tables 1 and 2.

Table 1. Values of variable factors for heat treatment of gelatin, their levels, intervals and limits of variation
Factors | Levels | Variation range
--- | --- | ---
Temperature, °C (x) | -1 0 +1 | 100 120 140 20
Heat treatment duration, hours (y) | 1/6 1/3 1/2 | 1/6

Table 2. Plan of the experiment on modelling of the heat treatment of fish gelatin

| Number of experiment | Conditions of experiment | x, °C | y, hours |
|---|---|---|---|
| 1 | 140 | 1/2 |
| 2 | 140 | 1/6 |
| 3 | 100 | 1/2 |
| 4 | 100 | 1/6 |
| 5 | 140 | 1/3 |
| 6 | 100 | 1/3 |
| 7 | 120 | 1/2 |
| 8 | 120 | 1/6 |
| 9 | 120 | 1/3 |

The study results can be used to optimize heat treatment modes using computer programs in an integrated programming environment for easy modeling and multiple computer experiments [9].

5. Discussion of the results
The dependence of the dynamic viscosity of a 10% fish gelatin solution on the temperature and duration of the heat treatment is presented in Table 3.

Table 3. Dependence of viscosity of fish gelatin solutions on the temperature and duration of the heat treatment

| Number of experiment | Input parameter | Particular output |
|---|---|---|
| | x, °C | y, hours | Solution viscosity, Pas |
| 1 | 140 | 1/2 | 64,4 |
| 2 | 140 | 1/6 | 43,8 |
| 3 | 100 | 1/2 | 39,9 |
| 4 | 100 | 1/6 | 38,9 |
| 5 | 140 | 1/3 | 61,3 |
| 6 | 100 | 1/3 | 39,0 |
| 7 | 120 | 1/2 | 44,7 |
| 8 | 120 | 1/6 | 38,9 |
| 9 | 120 | 1/3 | 43,8 |

As a result of the implementation of the orthogonal central composition plan of the two-factor experiment, the regression equation (formula 1) was obtained. It adequately describes the viscosity changes in fish gelatin solutions after the heat treatment:
\[ \eta = 225.67 - 3.309x - 78.6y + 1.47xy + 0.014x^2 - 105.6y^2, \quad (1) \]

where \( \eta \) is the solution viscosity, mPas; \( x \) is the treatment temperature, °C; \( y \) is the process duration, hours.

In order to evaluate the quality of the obtained regression equation, the determination coefficient was calculated, which characterizes the proportion of variation of the resultant attribute \( y \), explained by the regression (and, consequently, factor \( x \)), in the general variation \( y \). The determination coefficient \( R^2 \) takes values from 0 to 1. Correspondingly, the \( 1-R^2 \) value characterizes the share of variance \( y \) caused by the influence of other factors not taken into account in the model and specification errors.

The multiple determination coefficient was determined using the theorem of partition of sums of squares according to formula 2:

\[ R^2 = 1 - \frac{\sigma^2_{\text{res}}}{\sigma^2_y} \quad (2) \]

where \( \sigma^2_{\text{res}} = \frac{\sum(y - \bar{y})^2}{n} \) is the residual variance determined from the regression equation;
\[ \sigma^2_y = \frac{\sum(y - \bar{y})^2}{n} \] is the total variance of the resultant \( y \);
\( R^2 \) was determined using formula 3:

\[ R^2 = 1 - \frac{\sum(y - \bar{y})^2}{\sum(y - \bar{y})^2} . \quad (3) \]

The determinacy index for heat treatment of fish gelatin is \( R^2 = 0.963 \). Thus, the variation in the viscosity values of the fish gelatin solution by 96.3% is due to two analyzed factors (temperature and duration of heat treatment). The influence caused by other factors unaccounted for in the model is no more than 4%.

Graphical interpretation of the solution of the regression equation describing the dependence of the viscosity of fish gelatin solutions on temperature and duration of the heat treatment is presented in Figure 1.
Figure 1. Dependence of the dynamic viscosity of fish gelatin solutions on the temperature and duration of the heat treatment

Using this equation, reaction surfaces and isolines of its cross-section made in accordance with the equation, it was established that the lowest viscosity was obtained at the temperature of 110-120 °C and the heat treatment duration of 0.1-0.11 hours; the maximum viscosity of the solutions was obtained at the temperature of 140-145 °C and the heat treatment duration of 0.5-0.55 hours.
As a result of the study, it was found that the treatment of fish gelatin at the temperature of 95-110 °C does not lead to significant changes in the value of the dynamic viscosity index throughout the range of heat treatment duration. Rational mode of heat treatment of fish gelatin by physical and chemical characteristics (increase in the value of dynamic viscosity index more than 39 mPas) is the temperature range from 125 to 130 ºC. When the heat treatment temperature exceeds 130 ºC (temperature range from 135 to 140 ºC), there is an increase in duration of dissolution of fish gelatin (40-50 minutes) along with a significant increase in solution viscosity. This is quite justified when the dynamic viscosity of fish gelatin solutions increases and is confirmed by the physical and chemical bases of polymers. As the heat treatment temperature increases as a result of chemical and physical processes of the spatial network, there is a stage of intensive viscosity growth (up to the loss of fluidity) between reactive gelatin molecules. This process is caused by the increase in molecular weight and the formation of supramolecular structures of protein molecules of fish gelatin. It can be assumed that the process of physical structuring of fish gelatin, caused by the influence of temperature, goes deeper, accompanied by chemical structuring, i.e., the formation of transverse chemical bonds. Temperature affects the functional groups of gelatin by involving them in chemical reactions and the formation of a spatial network – cross-linking – which also increases the viscosity of gelatin solutions. During the heat treatment, not only intramolecular, but also intermolecular cross-linking and formation of polymer network can occur due to convergence of molecular chains caused by moisture loss [4].

There is also an increased fragility of fish gelatin leaf plates after heat treatment, which may indicate a spontaneous conformational transition of the fibrils and globules and the prevalence of globular tertiary conformations in the structure of the macromolecule, which determines the properties of fragility. As a result of this transition, the gelatin properties caused by fibrillar structures (elasticity, strength) disappear and the properties caused by globular structures (fragility) become stronger, while gelatin undergoes thermal destruction. The lower limit of thermal resistance of structured fish gelatin is in the range between 135 and 140 ºC. In addition, the appearance of an unpleasant odor is noted above this range. Conformational transformations of fish gelatin macromolecules occur without deep destruction of molecular structures and the rupture of the chemical bonds of the primary and secondary structure of gelatin, as evidenced by the fact of intensive viscosity increase with rising temperature.

Thus, reduced organoleptic characteristics, increased fragility and longer dissolution time degrade the consumer properties of fish gelatin. Therefore, for fish gelatin, the recommended high limit of thermostability of protein molecules is not more than 130 ºC, at which there is no thermal degradation and deterioration of the consumer properties of this consistency regulator.

6. Conclusion
Given there is complexity of the structural organization of fish gelatin, it should be noted that the influence of such a physical factor as temperature in the specified interval between 125 and 130 ºC during 20-30 minutes increases the values of the physical and chemical index of the dynamic viscosity of fish gelatin solution. In addition, it also improves the rheological properties of this structural agent. Modification of fish gelatin by heat treatment aims at improving its consumer properties and can be used in food and healthcare industries.

Modification of fish gelatin by heat treatment aims at improving its consumer properties and can be used in food and healthcare industries.

The novelty of the technological solution for the thermal modification of fish gelatin is confirmed by the Patent for the invention, No. RU2690437.

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