FUNCTIONAL-TECHNOLOGICAL PROPERTIES OF MEAT-AND-VEGETABLE EMULSIONS WITH THE ADDITION OF CHITOSAN DERIVATIVES

Irina Anatolyevna Shestopalova[1], Valentina Stepanovna Kolodyaznaya[1], Elena Ivanovna Kiprushkina[1], Elena Eduardovna Kuprina[1]*, Valentina Aleksandrovna Petrova[2], Elena Andreevna Rogozina[1], Veronika Olegovna Danko[1]

[1] ITMO University
(Saint Petersburg National Research University of Information Technologies, Mechanics and Optics)
Kronversky Avenue 49, St. Petersburg, Russian Federation;
e-mail: elkuprina@yandex.ru;

[2] Institute of Macromolecular Compounds of the Russian Academy of Sciences,
Bolshoi pr. VO 31, St. Petersburg 199004, Russian Federation

Abstract

This article provides data on the analysis of the properties of chitosan derivatives as a functional ingredient used in food technologies as a structure-forming agent, immunomodulator, enterosorbent of xantobiotics, anti-sclerotic and anti-arthritic factor, and as a regulator of the acidity of gastric juice.

The expediency of the use of N-methylallyl-chitosan (chitosan derivative) as a substance that improves the functional-technological (moisture and fat-retaining power) and rheological properties of meat-and-vegetable emulsions is shown.

The modes of micronising the emulsion depending on the chitosan derivative mass concentration, the speed of rotation of the knives of the microniser and the processing time were studied. Dependences on the change of moisture and fat-retaining power (MRP, FRP) and effective viscosity (η) on the above-mentioned parameters were investigated.

The parameters of micronising were validated: the speed of rotation of the knives (υ) was 2500 rpm, the processing time (τ) was 60 s, υ was 3000 rpm, and τ was 50 s; also, the mass fraction of chitosan derivatives was 0.06%, which ensures the production of meat-and-vegetable emulsions of high quality.

Key words: *chitosan derivative, meat-and-vegetable emulsion, functional-technological properties, rheological properties, micronising.*

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1. Introduction

In the process responsible for the production of meat-and-vegetable canned foods of emulsion type, the main and auxiliary raw materials are exposed to mechanical actions and heat treatments, affecting the functional-technological and rheological properties of the meat-and-vegetable emulsion, as well as the quality of the finished product.

The quality of the meat-and-vegetable canned foods of emulsion type as dispersion systems depends on the moisture-retaining power (MRP), fat-retaining power (FRP), and effective viscosity. To obtain a stable, high-quality emulsion, various emulsifiers and stabilisers have been proposed, of which chitosan and its derivatives have been less well-studied [1].

The wide use of chitosan in the food industry is due to its biological activity, moisture and fat-retaining capacities, as well as the ability to increase the value of the rheological characteristics of food masses [2, 3, 4].

The modification of chitosan by the introduction of allyl groups can increase its fat-holding and emulsifying ability, and the introduction of methyl groups increases the hydrophilicity of chitosan and its biocidal properties [5].

The primary amino groups of chitosan derivatives, or complexes, provide sorption properties including the binding of ions of heavy metals and radionuclides. Acting as a food component, chitosan derivatives improve the functional-technological and rheological characteristics of meat-and-vegetable emulsions and shows enterosorbent, immunomodulatory, anti-sclerotic and anti-arthrosis properties, as well as being a regulator of the acidity of gastric juice [3, 6].

The aim of the study was to investigate the change in the functional-technological and rheological properties of meat-and-vegetable emulsions, depending on the mode of micronising and the mass fraction of chitosan derivatives.

2. Materials and Methods

N-methylallyl-chitosan with a degree of quaternisation of 0.7 and a degree of substitution of 0.8 for allyl groups was used in this study.

For N-methylallyl-chitosan synthesis, chitosan with a molecular weight (MW) of $170*10^3$ was used; the degree of deacetylation was 0.8. The synthesis of N-methylallyl-chitosan was carried out in two stages. In the first step, the N-methyl-chitosan was synthesised via the N-alkylation reaction using a previously published method [7].

Chitosan was pre-activated by dispersing in water for 6 hours, after which the sample was filtered and washed with ethyl alcohol. The N-alkylation reaction was carried out in ethyl alcohol (1:20) in the presence of triethylamine (TEA) at 50°C for 12 hours, using methyl iodide (CH_3J) as an alkylating reagent. The molar ratio of the reactants chitosan/methyl iodide/triethylamine was 1:5:6. At the end of the reaction, the product was separated from the reaction mixture by filtration, washed with ethyl alcohol, and used for the following modification.

The degree of N-alkylation was calculated by the equation:

$$N = (1400-1400x) / (161 + 60x)$$

where:

N - amount of unbound amine nitrogen (determined according to the standard Van Slyka method),
14 - atom weight of nitrogen, multiplied by 100,
169.4 - molecular weight of the monomeric unit of chitosan (the degree of deacetylation 0.8),

60 - molecular weight of the CH_3 group multiplied by 4,
x - degree of quaternisation of chitosan.

The introduction of allyl groups (the second stage) was carried out by the nucleophilic substitution reaction of N-methyl chitosan by the procedure described [8].

Allyl bromide was used as the alkylating reagent. The reaction was carried out in a medium of 80% isopropyl alcohol (1:15), in the presence of sodium hydroxide solution, for 1 hour at 70°C, under the flow of nitrogen. The molar ratio of the reactants N-methylchitosan/sodium alkali/allyl bromide was 1:0.75:0.5. The resultant sample was purified by washing with 80% isopropyl alcohol until neutral reaction, then with acetone and dried *in vacuo* without heating.

The number of allyl groups was determined by the standard method of determining the bromine number (Knopp's method). The degree of substitution was calculated using the equation:

$$\text{Br-number } (\%) = 15984x / (M + 41x),$$

where:
159.84 - molecular weight of the molecule Br_2 multiplied by 100,
201.9 - molecular weight of monomeric unit of N-methylchitosan (with degree of quaternisation of 0.7),
41 - is the molecular weight of the allyl group,
x - is the degree of substitution, multiplied by 100.

The object of the study was to produce a meat-and-vegetable emulsion according to two recipes. Recipe No.1 included manually deboned chicken meat as the main raw material, along with Bulgarian pepper, beans, soy isolate, pork fat, vegetable oil, chitosan derivatives and flavour additives. Recipe No. 2 included manually deboned chicken meat and semi-fat pork as the main raw materials, along with carrots, lentil, soy isolate, vegetable oil, chitosan derivatives and flavour additives.

The rheological properties of the emulsion (η) were investigated with the help of the "Rheotest-2" rotational viscosimeter, and functional-technological properties (MRP, FRP) according to the methods described in [9].

3. Results and discussion

Micronising of the meat-and-vegetable emulsion was carried out at the rotational speed of the knives (υ) of the Grindomix GM200 unit from 2000 to 4000 rpm and with a time (τ) from 30 to 70 seconds; the final temperature of the meat emulsion did not exceed 12-1400^{0}C.

It can be seen from Fig. 1 and 2 that the maximum values of MRP and FRP correspond to the micronising at the rotational speed of the knives of 2500 and 3000 rpm for the meat-and-vegetable emulsions prepared according to recipes No. 1 and 2, respectively. Furthermore, with the increase in the number of revolutions, a reduction of these functional-technological properties occurred.

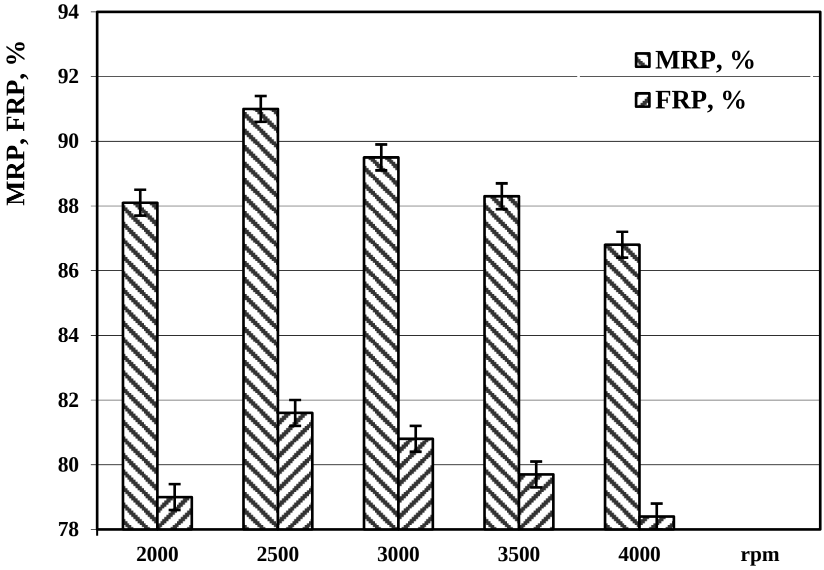

Figure 1. Dependence of MRP, FRP on the modes of micronising of the meat-and-vegetable emulsion (recipe №1)

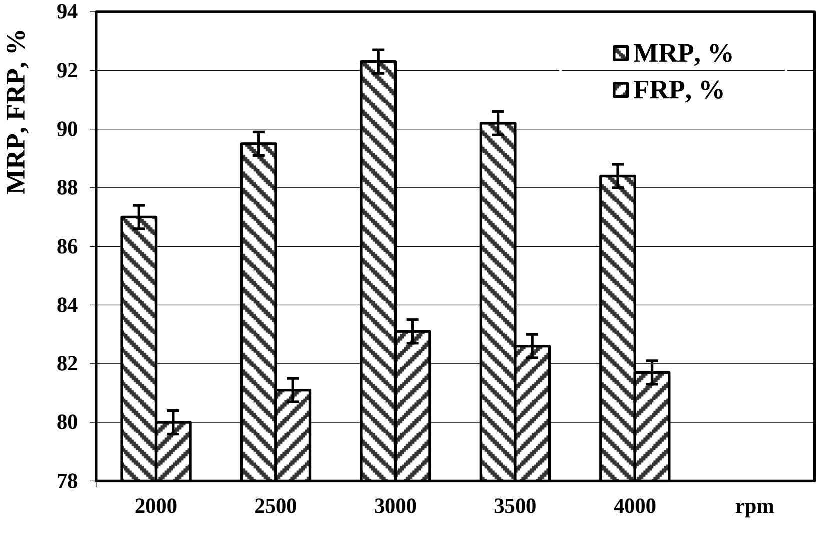

Figure 2. Dependence of MRP, FRP on the modes of micronising of the meat-and-vegetable emulsion (recipe №2)

When processing the meat-raw material in the first stage, the mechanical destruction of tissues occurred, along with a decrease in the yield of proteins, their intensive swelling, an interaction between themselves and added water, and the formation of the spatial matrix protein. Further micronising led to the dispersion of fat, a reduction in the linear dimensions of the morphological elements of the emulsion, and the mixing of components of the forcemeat, which provided a stable water-protein-fat emulsion. However, the degree of micronising should have been sufficient to provide the necessary amount of water- and salt-soluble proteins to cover the dispersed fat particles, since they are the material basis for the formation of the continuous framework after being thermally coagulated, which ultimately provides the structure of the finished product.

The period of chopping, lower or higher than normal, led to a decrease in the functional-technological and rheological properties of the meat-and-vegetable emulsion.

Thus, a short period of chopping does not provide the necessary degree of micronising of the raw material, the yield of protein into the minced system and efficient mixing. In contrast, a higher-than-normal chopping period leads to the formation of very small droplets of fat that are less resistant to the friction resistance of the liquid phase than larger ones. Consequently, during heat treatment, the droplets are reconnected to larger ones, with the release of fat and broth from the product. Moreover, with too fine micronising, the number of fat globules increases and their total surface area increases as well. This requires a large quantity of dissolved protein to stabilise the fat-water system [10].

Fig. 3 and 4, given in double logarithmic coordinates, show the graphical relationship between the effective viscosity and the gradient of the shear rate (γ) of the meat-and-vegetable emulsion with a change in its values from 0.33 to 145.8 s^{-1}.

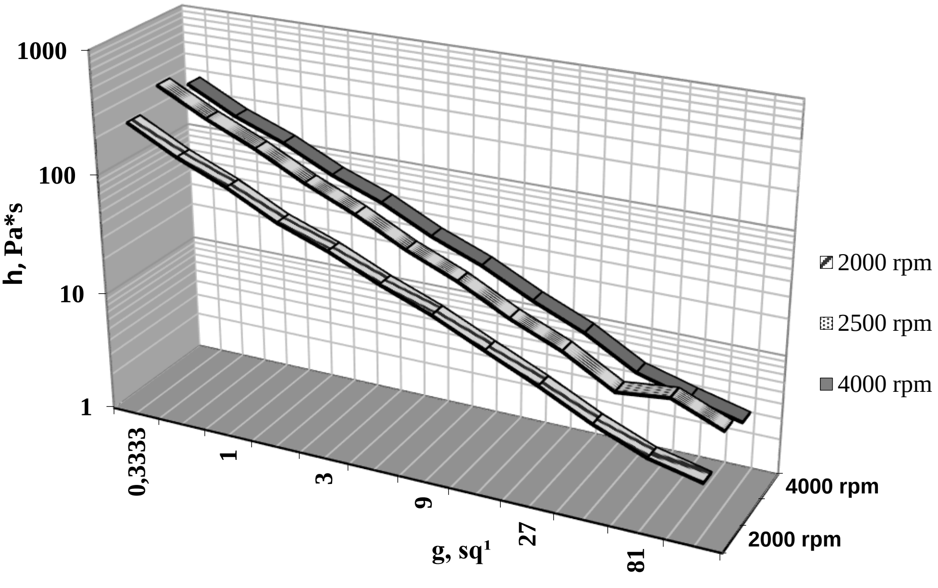

Figure 3. The flow curve of the meat-and-vegetable emulsion at different regimes of micronising (recipe №1)

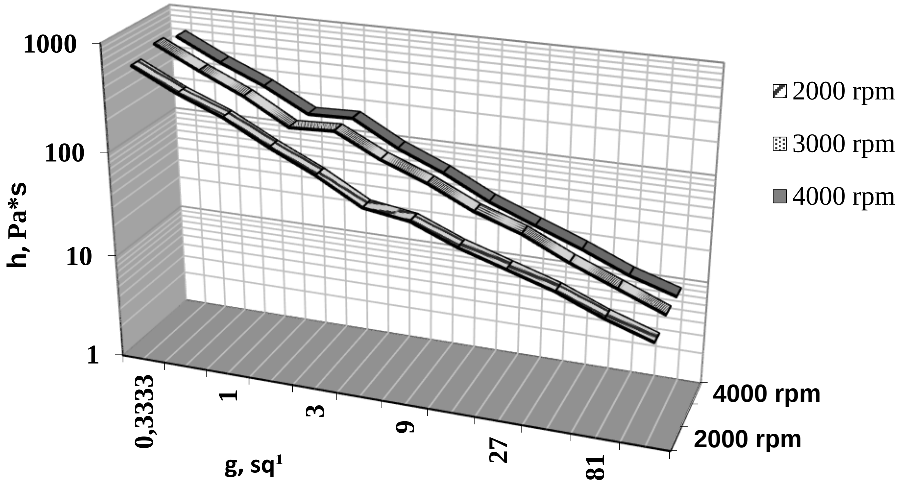

Figure 4. The flow curve of the meat-and-vegetable emulsion at different regimes of micronising (recipe №2)

The maximum viscosity of the meat-and-vegetable emulsion for canned foods prepared according to Recipe No. 1 is 383.8 Pa*s, while it is 720.8 P*s for canned food prepared according to Recipe No. 2, with a gradient of shear rate of 0.33 s^{-1}, and rotation speed of the knives of 2500 and 3000 rpm, respectively. At these speeds, the effective viscosity of the meat-and-vegetable emulsion decreases as the velocity gradient increases from 0.33 to 145.8 s^{-1}.

A significant reduction in the effective viscosity of the meat-and-vegetable emulsion at a constant temperature is due to the fact that it possesses the properties of pseudoplastic materials, in which the effective viscosity lowers with an increasing gradient of shear rate. As the gradient of shear rate increases, the asymmetric molecules of the material undergo ordering, since they are located along a longer axis in the direction of the flow. This leads to the unfolding of coils of macromolecules in the chain of the protein molecule, which leads to the destruction of the structural framework of the system and its individual elements; as a result, the macromolecules become easily streamlined and the effective viscosity of the meat-and-vegetable emulsion falls down.

In addition, during micronising, the intensive destruction of particles of meat and vegetable raw materials occurs, the total surface of the particles increases, moisture from the free-state transfers to the surface-bound state, and a new structure is formed in which the particles swell and go into an amorphous state.

However, with an increase in the rotation speed of the knives of the microniser from 2000 to 4000 rpm, the macrostructure of the meat-and-vegetable system is increasingly destroyed, a result of which is that the amount of releasing moisture is increased; therefore, the effective viscosity of the emulsion at the rotation speed of the knives of more than 2500 and 3000 rpm for recipes №1 and №2, respectively, is decreased [10].

The influence of the mass fraction of chitosan derivative (C, %) introduced into the meat-and-vegetable emulsion in the form of solution in 1% citric acid, on its functional-technological and rheological properties was studied.

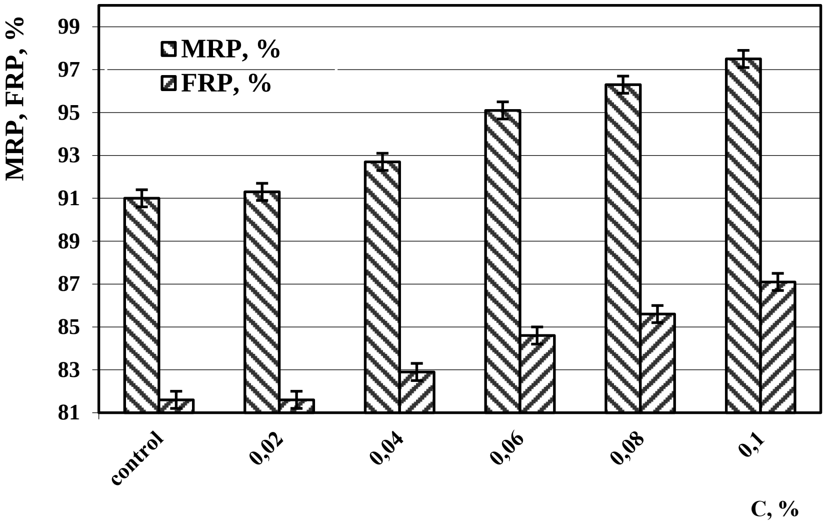

Figure 5. Dependence of MRP, FRP on the mass fraction of chitosan derivatives (recipe №1)

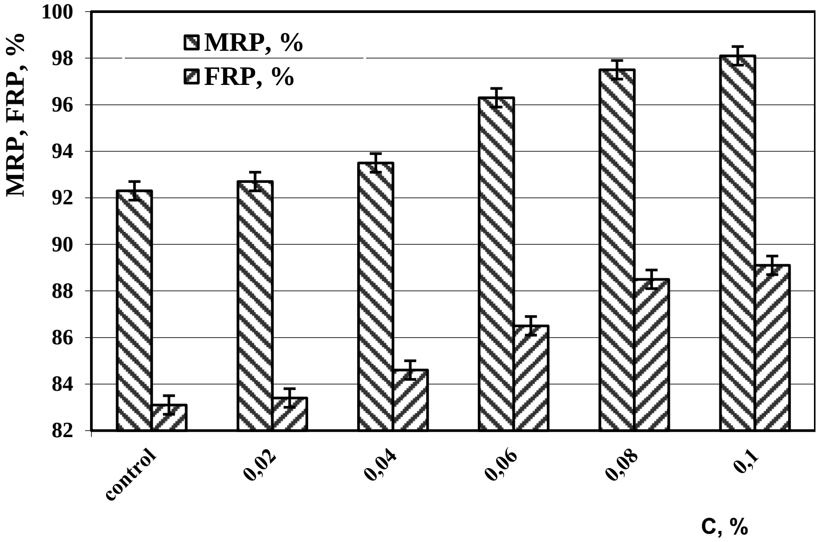

Figure 6. Dependence of MRP, FRP on the mass fraction of chitosan derivatives (recipe №2)

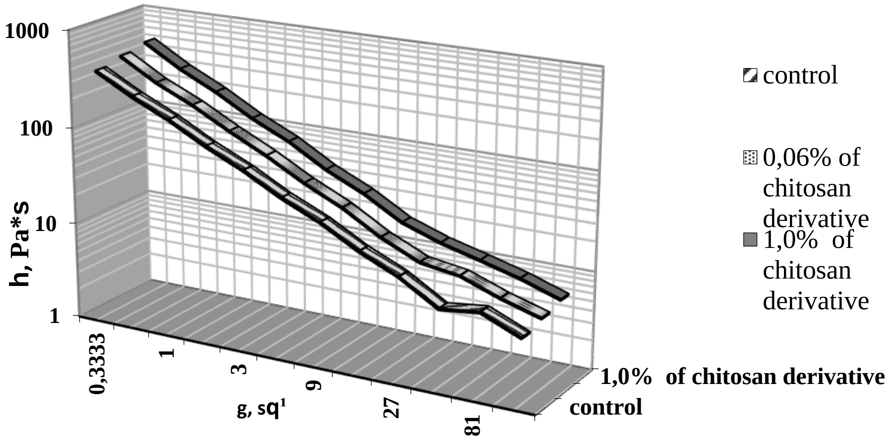

Figure 7. The flow curve of the meat-and-vegetable emulsion at different mass fractions of chitosan derivatives (recipe №1)

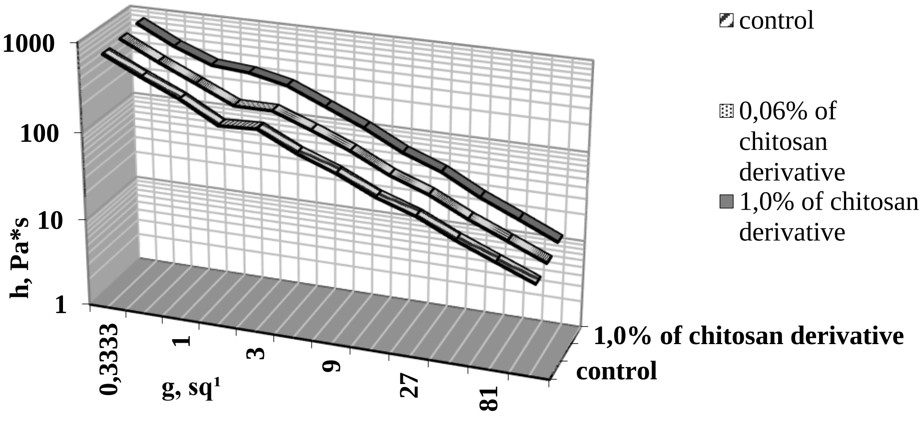

Figure 8. The flow curve of the meat-and-vegetable emulsion at different mass fraction of chitosan derivatives (recipe №2)

When considering the changes in the MRP, FRP and η, as shown in Figures 5, 6, 7 and 8, it follows that these values go up with an increasing mass fraction of chitosan derivatives. Chitosan derivatives, which are high-molecular substances, stabilise the meat-and-vegetable emulsion, which is stipulated by the special structural and mechanical properties of the adsorption interphase layers, which are formed when the polar groups of the protein are oriented to water, and the nonpolar ones to oil. From a physicochemical point of view, an increase in the effective viscosity is achieved due to the formation of basic and additional types of bonds between molecules: ionic and hydrogen bonds.

Despite the fact that the functional-technological and rheological properties improve with an increasing content of the introduced chitosan derivative, the mass fraction of 0.06% is the optimal amount, since its further increase leads to an undesirable change in organoleptic parameters - an astringent taste is observed.

Thus, the optimal modes of micronising are υ = 2500 rpm, τ = 60 s and υ = 3000 rpm, τ = 50 s and the chitosan derivative mass fraction is 0.06% for the meat-and-vegetable emulsions made according to recipes No. 1 and No. 2 respectively.

4. References

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