



IMPROVED FREEZING TECHNOLOGY OF MINCED MEAT PRODUCTS IN BIOPOLYMER PACKAGING MATERIAL

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ABSTRACT

This work is aimed at determination and selection of optimum conditions for freezing minced meat products in polymer packing. A new freezing method in biopolymer packaging material is proposed for minced meat products. Strength properties of CornBag biopolymer film upon freezing and low temperature storage have been studied. It has been established that this film can be used for freezing and low temperature storage of food products. The methods of convective, contact, and combined freezing have been experimentally studied with preliminary packing of minced meat products in biopolymer vacuum packaging material. It has been detected that freezing of packed products makes it possible to eliminate shrinkage of products, oxidation of lipid fraction, and organoleptic properties are retained. Graphic analytic procedure is proposed for prediction of freezing duration of minced meat products. Storage mode for minced meat products at 18°C for six months has been selected. Improved freezing technology is comprised of combined convective air blowing and contact freezing on plate with preliminary packing into biopolymer vacuum package.

Keywords: lipid fraction, biopolymer fraction, combined freezing, moisture crystallization, vacuum packaging.

INTRODUCTION

Meat products are perishable, in order to increase their storage life and to use as food all the year round irrespective of season, they should be specially processed. Freezing is the most efficient for processing and storage of meat and meat products, since it allows compensating seasonality of animal products, while preserving their biological and nutritional value during long time [1]. This conservation method is sufficiently common and economic, it results in minimum modifications of initial properties of food products, prevents spoilage, retains nutritional value and consumer properties.

Conservation by freezing is based on the principles of anabiosis, when biochemical activity of tissue enzymes is inhibited and activity of microorganisms is suppressed. Upon freezing, enzymatic hydrolysis of proteins in raw animal material is decelerated at -18°C and the temperature decrease to -25°C leads to decrease in the rate of enzymatic hydrolysis and oxidation of tissue lipids. When meat and meat products are frozen below cryoscopic point, phase transfer of water into ice is initiated. Distribution of ice crystals in meat and their sizes depend on freezing conditions as well as composition and properties of raw products [2]. During refrigerated storage of frozen meat products there occur physical, chemical, and biochemical modifications. Thus, upon long-term storage, there occur recrystallization, evaporation and sublimation of water, dewatering and shrinkage of meat surface. In its turn, this leads to modification in fat and lean tissues [3, 4]. Denaturation and hydrolysis modifications of proteins are most peculiar for lean meat, and in fat tissues, hydrolysis and oxidation of lipids occur

[5, 6]. The authors [7-9] compared temperature regimes of maturing and storage of beef fillet (-12°C and -18°C), quality variations were detected; estimation of bacterial content of meat products was required for each regime.

The above-mentioned processes, affecting negatively the quality of minced meat products, can be significantly inhibited by freezing of packed semi-finished products. In order to provide maximum possible quality retention of the products, the applied packaging materials should provide minimum weight loss during storage (shrinkage), that is, to be characterized by low level of moisture permeability. Such materials include aluminum foil, aluminum foil with polyethylene, polyethylene, polypropylene, double-sided paraffin paper, paperboard with polyethylene, cellophane with polyethylene, polystyrene, paper with polyvinyl acetate [10].

Another important requirement to packaging materials of frozen products is gas impermeability. Packaging material should not only protect products against air oxygen but also preserve volatile aromatic substances. In order to decrease oxidation activity causing deterioration of consumer properties, it is required to constrain access of oxygen to product surface. This is aided by vacuum packaging or replacing air in package with nitrogen [11] and various gas mixes [12]. Bacterial activity is suppressed by active packages including nanocomponents capable to increase expiry date of meat products. Tornuk F., Hancer M., Sagdic O., Yetim H propose to apply essential oils as nanocomponents, which are characterized by antimicrobial action, in combination with conventional material: linear low-density polyethylene [5]. Wronaa M., Nerina C, Alfonsob M.,



Caballero M. used capsules with extract of green tea as antimicrobial constituent of polyethylene package for minced meat [13].

Any package has its lifecycle comprised of three main stages: fabrication, usage, and recycling [11]. The most suitable variant of package in terms of recycling is the package capable to be decomposed in the shortest times without harm to environment. Such requirements are met by package made of biopolymers [14-16], as well as various "eatable" films of plant components [17, 18]. Biopolymers are usually fabricated by polymerization of raw biological materials. Such raw materials are either extracted from plants and animals, or synthesized using advanced commercial technologies [15, 19]. At present, the use of biopolymers in packaging materials is constrained, since their behavior under low temperatures and long-term storage of products has been studied insufficiently.

As mentioned above, low-temperature treatment can significantly influence the quality of meat products, thus, it is very important to control freezing and to select correctly refrigerating equipment. The authors in [20] describe thermal model of freezing duration of food products of various shape and sizes, this model can be used for selection of refrigerating equipment. The authors [21] have developed model of heat and mass exchange during freezing, which considers for heat transfer, crystallization, transfer, evaporation, and sublimation of water. The model allows forecasting freezing time and weight loss for predefined nonporous product and predefined freezing mode. It was reported that the minimum weight loss was observed upon cryogenic freezing at -100°C . Under commercial conditions, this temperature regime is not used due to unreasonably high expenses. The authors in [7], aiming at optimization of time and temperature, studied freezing of beef meat on refrigerated plate using model based on the Planck equations. Laboratory simulation was carried out with a lump of beef of various sizes and thickness. Freezing plots were described on the basis of thermal and physical properties of beef, i.e. specific thermal capacity, heat conductance, and density.

However, the aforementioned models of freezing do not account for heterogeneous properties of minced meat products, thus, are not suitable for prediction of the processes with accounting for plant constituent in meat roulade (zrazy), as well as do not account for the existence and behavior of packaging material upon freezing.

As demonstrated in publications, freezing technologies and low-temperature storage of minced meat products were not sufficiently analyzed and should be studied additionally with consideration for components of the products. In this regard, this work is aimed at determination of optimum freezing conditions of minced meat products stuffed with vegetables in biopolymer packaging material.

METHODS

The subject of research was minced meat products stuffed with vegetables: zrazy. The minced meat was made of beef, quality grade I, onion and spices. The vegetable stuff was made of Siberian fruits and vegetables: carrot, bulb onion, parsley root, celery root, garlic, fennel.

The meat products were packed into biopolymer film: CornBag (Olive Green Pte Ltd, Singapore) made of Origo (corn and batata starch). The CornBag packages are characterized by the recommended temperature range of operation from -20°C to 40°C . According to producer specifications, when respective conditions are met (temperature, moisture, and existence of microbes), the decomposition time is 90 days [22]. In addition, the products were packed into biaxially oriented polypropylene film (BOPP).

Physical properties of films were tested on a XLW(M) tension machine (Labthink Instruments Co., China, 2011). The measurement error was 1% from measured accuracy. The tension machine has seven operation modes. The following tests were performed: testing of tension strength and relative elongation upon rupture. The machine firmware performs statistical analysis of a sample group, superposition of test curves and data comparison with history, as well as setting parameters, printing, cleaning and calibration, etc. Specifications of the tension testing machine are summarized in Table-1.

Table-1. Specification of XLW (M) automatic tension testing machine.

Parameter	Value
Force measuring sensor, N	300 N
Rate of extension, mm/min	from 50 to 500
Stroke of yoke, mm	600
Gas pressure, MPa	0.5-0.7
Dimensions, mm	450×580×1,100

The tests using tension machine were performed with samples of biopolymer and polypropylene films with the width of 20 mm and the length of 200 mm, the thickness of the samples was 0.002 mm. The distance between clamps of the tension machine was 110 mm. The rate of motion of the upper clamp with regard to the lower one was 300 mm/min. Preliminary prepared sample was installed between the two clamps, which moved in appropriate directions during tests. Signals of force and position were separately recorded by dynamometer, fixed on movable clamp, and internal sensor of position, respectively. Tension strength, rupture strength, and deformation rate were calculated using firmware of the tension machine.

Organoleptic properties of minced meat products in fresh and frozen state were estimated by the developed procedure of estimation of organoleptic properties using



five-score system on the basis of State standard GOST 32951-2014 [23]. This document defines which organoleptic properties of minced meat products, quality grade B (with lean tissue in the recipe from 60 to 80 wt %, inclusively), should be satisfied, namely: appearance of product cross section, color, smell, and taste after thermal treatment.

Content of vitamin E was determined according to State standard GOST 32307-2013 using high-efficiency liquid chromatograph [24].

Thermal and physical properties of fresh and frozen minced meat products were determined by the first buffer method of two temperature and time intervals [25].

The temperature of minced meat products was measured by chromel-copel thermocouples, analog input measurement unit MVA8 (OVEN Co., Moscow, 2013), analog digital converter AC-4 (OVEN Co., Moscow, 2015). The acquired temperature measurements were stored in .log format, then the data were processed in Microsoft Excel.

Freezing was performed on the proprietary laboratory rig (Figure-1), comprised of the cooling chest 1; the tunnel with metal plates 9, the tunnel with metal grid 10; the instruments for temperature measurements [26].

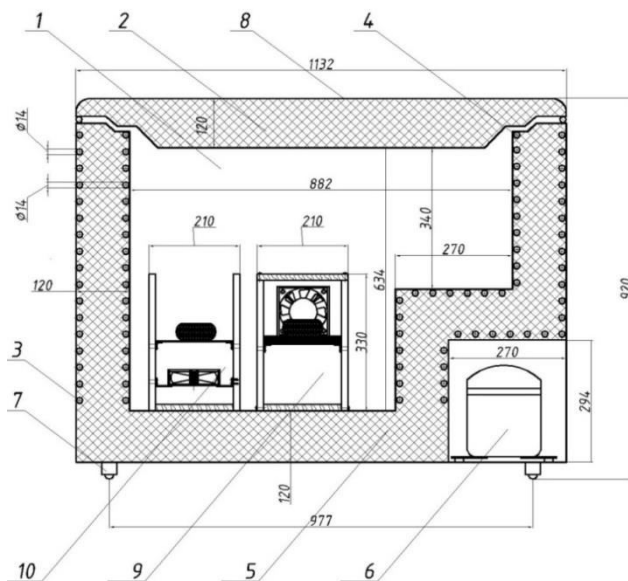


Figure-1. Laboratory bench: 1 - internal chamber; 2 - cooling chest lid; 3 - condenser; 4 - vaporizer; 5 - insulating layer; 6 - compressor; 7 - wheel support; 8 - casing; 9 - tunnel with metal plates; 10 - tunnel with metal grid.

The thermocouples, connected to temperature instruments, were installed on the surface and the center of product. The thermocouples were made under laboratory conditions and calibrated individually. With this aim, the thermocouple juncture was placed into a Dewar's flask with melting ice at about 0°C.

The obtained calibration is summarized in Table-2.

Table-2. Calibration of measurement system.

Number and designation of thermocouple	Adjusting coefficient, °C	Measurement accuracy
KhK TP No.1	0.3°C	± 0.05°C
KhK TP No.2	0.4°C	
KhK TP No.3	0.5°C	
KhK TP No.4	0.4°C	

Rapid freezing of minced meat products in vacuumed biopolymer package in the tests was performed in shrink polypropylene bags with the aim of convenient installation of thermocouples into the product center and on the product surface [27]. Minced meat products were packed under vacuum using a V110RP one chamber vacuum machine (Elega, China, 2017). Thermal shrinkage of polypropylene film was performed using a MINIMA EVO shrink wrap machine (Minipack-Torre, Italy, 2017).

The product was placed in the tunnels 9 and 10 depending on the considered freezing method. The cooling chest was covered; the fan of respective tunnel was switched on. When the preset temperature in the product center was reached, the fan was switched off. The laboratory bench was equipped with 17 W fans, capable to generate air flow rate from 1 to 3 m/s. The temperature regimes were preset using a Comfort controller of the cooling chest, the preset temperature was shown in external display. Analog signals from measuring sensors proportional to measured variables were converted into digital form in MVA8 and AS4 modules and transferred to PC for storage and further processing.

RESULTS

Freezing of minced meat products is performed at the temperatures below -20°C, in this regard the authors analyzed possibility to use CornBag packages to freeze food products at -20°C, -40°C, and -60°C, which was significantly lower than the recommended range. The packages were stored at the mentioned temperature during 1, 2, and 3 months. Experimentally determined rupture strength σ_{exp} , MPa, and elongation ξ_{exp} , % (Table 3) were processed by correlation and regression analysis in Microsoft Excel, Eqs. (1) and (2) were obtained for description of these variables as a function of time n , months, and storage temperature t , °C.

$$\sigma = \sigma_0 + 0.42 \cdot t - 12.02 \cdot n \quad (1)$$

$$\xi = \xi_0 + 0.376 \cdot t - 10.53 \cdot n \quad (2)$$

where $\sigma_0 = 475.72$ MPa was the initial rupture strength of film at $t = 0^\circ\text{C}$; $\xi_0 = 415.67\%$ was the initial elongation of film at $t = 0^\circ\text{C}$.



Table-3. Comparison of experimental and calculated strength properties of biopolymer film.

$\xi_{exp}, \%$	$\xi_{calc}, \%$	$\Delta\xi, \%$	σ_{exp}, MPa	$\sigma_{calc}, \text{MPa}$	$\Delta\sigma, \%$
Relative elongation			Rupture strength		
405.13	414.45	2.30	479.74	474.10	1.17
388.50	403.92	3.97	470.63	462.08	1.81
385.37	393.38	2.08	443.68	450.06	1.46
402.44	406.92	1.11	470.51	465.56	1.05
384.25	396.39	3.16	463.80	453.54	2.21
381.44	385.86	1.16	421.54	441.52	4.75
393.89	399.40	1.40	468.62	457.03	2.47
379.54	388.87	2.46	430.99	445.01	3.27
367.48	378.33	2.95	426.79	432.99	1.47
Average error, %		2.3	Average error, %		2.18

The obtained equations allowed to plot response surfaces showing variation of rupture strength and tension during film storage at low temperatures (Figures 2, 3).

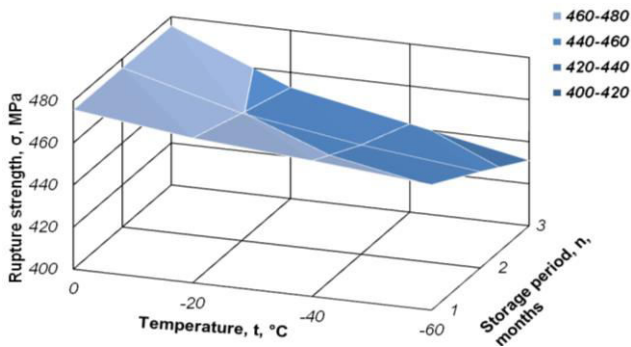


Figure-2. Rupture strength of biopolymer film as a function of temperature and storage time.

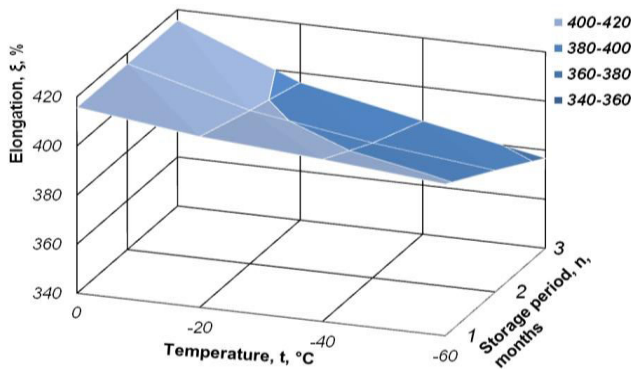


Figure-3. Elongation of biopolymer film as a function of temperature and storage time.

Comparison of experimental (ξ_{exp} and σ_{exp}) physical properties of biopolymer film with their calculated values (ξ_{calc} and σ_{calc}) obtained by Eqs. (1) and (2) is summarized in Table-3.

Figure-4 illustrates comparative analysis of properties of biopolymer and BOPP films.

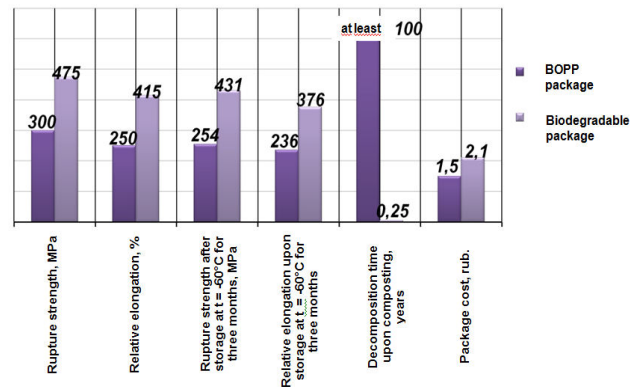


Figure-4. Comparative analysis of biopolymer and BOPP films.

The next stage of the studies was devoted to analysis of freezing method of minced meat products packed into biopolymer film. Freezing was performed using three methods: convection in air flow, contact on metal plate, and combined procedure comprised of preliminary freezing in ascending air flow and final freezing on metal plate. The freezing rates of minced meat products according to two temperature regimes are summarized in Table-4.

Table-4. Freezing rate.

Freezing method	Freezing rate	
	-30°C	-40°C
Convective	0.59	0.59
Contact	0.83	0.83
Combined	0.77	0.77



Rational freezing parameters of minced meat products using the new combined method were analyzed.

Figure-5 illustrates the temperature of minced meat products as a function of time at -30°C and -40°C .

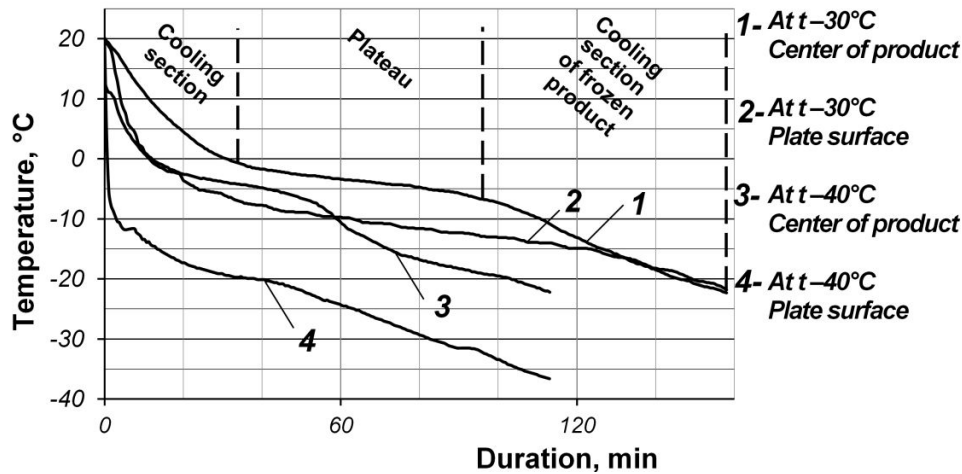


Figure-5. Curves of freezing of minced meat products by combined method.

On the basis of the experimental results, the authors proposed graphic and analytical prediction of freezing duration of minced meat products using the combined method based on the concept of movement of interface between solidified and liquid phases from periphery into the bulk during heat extraction from its surfaces (Figure-6). The predictions accounted for the fact that the vegetable stuff with the thickness of 8 mm was surrounded by a layer of minced meat with the thickness of 6 mm. The thickness of packed crazy was 20 mm. The

lower crazy layer in packaging material would be frozen due to heat transfer to the metal plate, the upper layer would be frozen due to heat transfer to horizontal flow of cold air at the rate of 1.5 m/s. Freezing of packed crazy was terminated when the boundaries of the upper and the lower layers contacted with each other, i.e. the minced meat product was completely frozen. The thicknesses of these two layers and the time required for their freezing were calculated using the Planck equation [7].

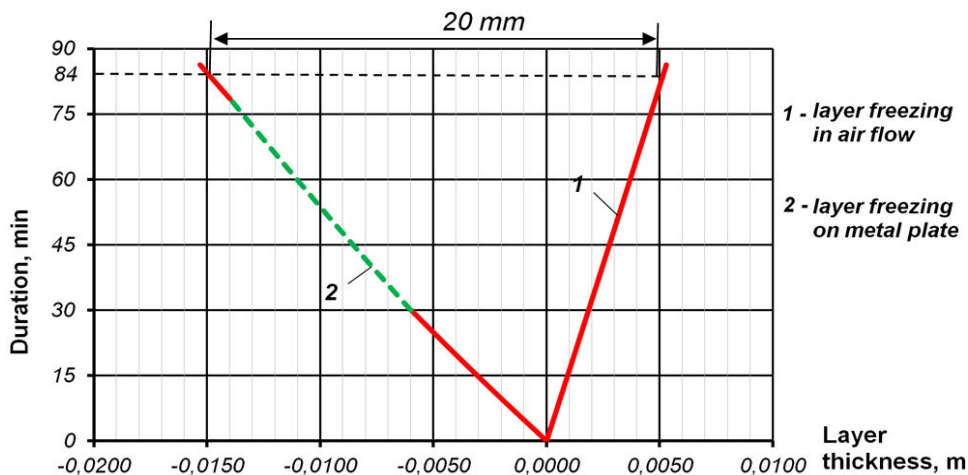


Figure-6. Duration of freezing by combined method.

Organoleptic properties of crazy frozen without packaging material and packed into biopolymer film were compared. The analyzed samples were numbered as follows: 1 - freezing of packed products at -30°C ; 2 - freezing of packed products at -40°C ; 3 - freezing of unpacked products at -30°C ; 4 - freezing of unpacked products at -40°C . The frozen crazy were stored during six months at -18°C . On the basis of assigned scores, the

linear diagram was plotted depicting organoleptic estimation of all samples (Figure-7). The minced meat products were fabricated at Healthy Nutrition research and production association, Kemerovo (Russia). The members of the taste panel were the Director of Healthy Nutrition research and production association, Chief Technologist, and the authors of this article.

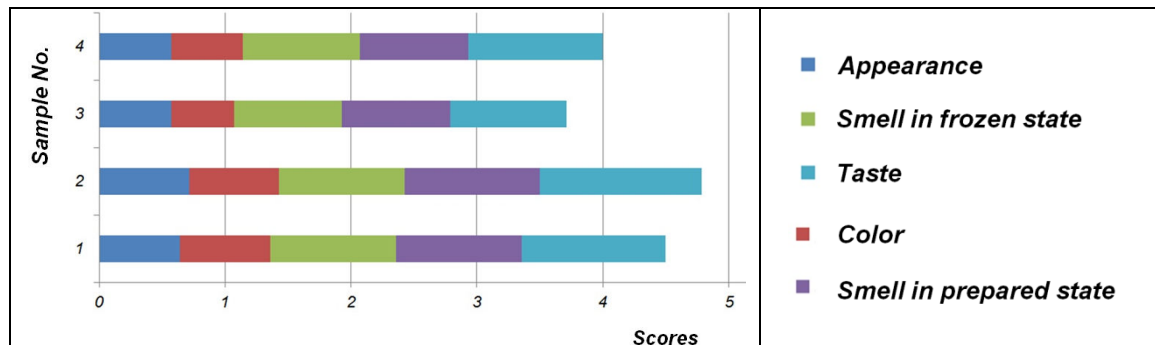


Figure-7. Organoleptic quality estimation of crazy stuffed with vegetables.

The content of vitamin E in the minced meat products was determined immediately after freezing equaling to $0.47 \mu\text{g}/100 \text{ g}$. After storage for six months, the content of vitamin E slightly decreased: $0.43 \mu\text{g}/100 \text{ g}$.

DISCUSSIONS

The analysis of low-temperature impact on such physical properties of biopolymer film as rupture strength and tension demonstrated that these properties decreased less than by 10% during storage at -60°C in three months. This evidences that low-temperature impact did not influence significantly strength properties of biopolymer film, hence, CornBag biopolymer packages can be used for packaging and subsequent freezing in the range from -20°C to -60°C and storage of food products during six months, in our case: minced meat products.

According to Table-3, the experimental and the calculated strength properties of biopolymer film varied insignificantly, average error was less than 3%. Therefore, the developed Eqs. (1) and (2) based on correlation and regression analysis, describing strength properties of biopolymer film as a function of storage temperature and time, could be applied for prediction of these properties in predefined temperature and time ranges.

Comparative analysis of properties of biopolymer and BOPP films (Figure-4) demonstrated that the biopolymer film was superior to the BOPP film in terms of strength properties; moreover, it was characterized by significantly lower decomposition time with lower harm to environment.

At the next stage of studies, the fabricated minced meat products (zrazy) were placed into biopolymer package, vacuumed, and sealed. Then the packed batch of zrazy was sent to freezing. As already mentioned, the minced meat products packed into biopolymer film were frozen by three methods. According to Table-4, the highest freezing rate was observed for the contact method. However, this method had certain disadvantage: even minor content of moisture on packaging material before freezing led to adherence of packaging material to plate surface. This could be avoided by combined freezing method.

In further studies, the zrazy were frozen by the combined method. The curve of freezing by the combined method illustrated in Figure-5 presents temperature on the

surface and in the center of packed zrazy as a function of duration of low-temperature treatment; it is comprised of three segments, which characterize freezing stages. Let us consider the curve 1, comparing its pattern with standard plot of freezing of food products. At the first freezing stage during 40 min, the product was cooled accompanied by intensive drop of its temperature. The second segment (about 1 h) was characterized by moderate temperature decrease in the range of 10°C , presenting the plateau; at this stage, moisture in the zrazy was intensively crystallized. At the third stage (about 1h), the frozen zrazy were cooled, which was accompanied by crystallization of minor amount of moisture, usually physically and chemically bonded [28]. Freezing duration at -40°C in cooling chest was 85 min (curves 3 and 4); the freezing rate was 1.33 cm/h .

The proposed graphic and analytic prediction procedure of freezing duration (Figure-6) made it possible to calculate freezing time of minced meat products (zrazy) by combined method. The predicted freezing duration was 84 min (Figure-6), which corresponded to the experimental data (Figure-5, curves 3 and 4). The layer thickness of minced meat product, frozen under the action of cold air flow, was 5 mm, and of that frozen on metal plate was 15 mm (Figure-6).

Analysis of organoleptic properties of minced meat products, frozen under various conditions, demonstrated that superior taste estimates were characteristic for the zrazy after freezing at -40°C by combined method with preliminary packing in biopolymer film (Figure-7). The worst estimates were obtained by the zrazy frozen at -30°C by contact method without packing. Obtained organoleptic estimates corresponded to the published data [3, 4, 29]. Product, frozen and stored in packaging material, is not exposed to shrinkage, lipid fraction is significantly slower [29], which allows fabricating product with superior organoleptic properties. Moreover, as mentioned by Dalvi-Isfahan M., Jha P. K., Tavakoli J., Daraei-Garmakhany A., Xanthakis E., Le-Bail A [4], the freezing temperature influences the morphology of ice crystals (size, number of crystals, their shape and distribution), thus influencing the microstructure of frozen products. At -40°C , the ice crystals generated in product have finer structure, which promotes lower damage to cell structure of minced meat and vegetable stuff, improved



freezing, as well as better organoleptic properties of frozen product.

According to Holman Benjamin W.B., Ponnampalam Eric N., Kilgannon Ashleigh K., Collins Damian, Plozza Tim, Hopkins David L., quality properties can be estimated by comparison of the content of vitamin E under various storage modes of minced meat products. Insignificant content variation of vitamin E in samples evidences the absence of lipid oxidation [30]. The obtained data demonstrated that the loss of vitamin E was about 10%, which evidenced the absence of lipid oxidation.

Therefore, application of biopolymer vacuumed package allows to protect reliably the product against moisture loss and to retain its organoleptic properties.

CONCLUSIONS

Improved combined technology of low-temperature conservation and long-term storage of minced meat products packed in biopolymer film has been developed, characterized by absence of product shrinkage, minimization of bacterial content, and retention of organoleptic properties. It has been established that the decrease in strength properties (rupture and tension strength) of CornBag biopolymer film stored at -60°C for three months is lower than 10%, which evidences possibility of its application for freezing and low-temperature storage of food products, including minced meat products.

The combined method of freezing of minced meat products in biopolymer film has been developed, including preliminary freezing of product packed in vacuum on grid substrate and final freezing on metal refrigerated plate, which excludes freezing-on and damage of packaging material upon separation from the plate.

Graphic analytic model of freezing of minced meat products has been developed. The mode of combined low-temperature treatment and storage of minced meat products packed into biopolymer film has been selected. Freezing conditions are as follows: -40°C , 85 min, 1.33 cm/h. Storage temperature is -18°C .

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