STUDY OF THE POSSIBILITY TO USE POLYMERIC MATERIALS WITH BARRIER PROPERTIES FOR THE PACKAGING OF FISH PRODUCTS

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In recent years the food safety question became very critical in Russia. One of the main problems facing the fish industry is the retention of the quality and safety of the water bioresources and food, produced from them.

To solve this problem, new technologies are developed and applied in industry; at the same time, scientists improve old traditional technologies, which make it possible to manufacture production, characterizing not only by good organoleptic features, but also by the high food value and stable microbiological parameters during the whole shelf life of the product.

A packaging material, based on polymeric materials with barrier properties, is characterized by low oxygen and carbon dioxide transmission coefficients (cm3/m3 per 24 h); this fact makes it possible to significantly delay and/or suspend the hydrolytic and oxidative processes in proteins and lipids and to prevent the microbiological contamination of a product. In addition, the use of such materials for the packaging not only protects the product against any environmental influence, but also reduces its natural storage losses.

According to statistical data, the use of different kinds of packaging for fish products increased every year. However, comparing to the other branches of the food industry, the percentage of the packaged fish products on the Russian market still remains rather low.

In our opinion, the use of domestic polymeric materials with barrier properties seems to be relevant concerning the retention of the quality and safety of fish products.

The purpose of our study was to investigate the possibility of the use of polymeric materials with barrier properties for the packaging of a fish production in a gas-modified medium.

The object of our study was a filleted Atlantic salmon (*Salmo salar* L.); the weight of pieces did not exceed 0.2 kg.

The fish was packed into a five-layer polymeric co-extrusion film, having a barrier layer. The film was manufactured by the "Polimery XXI veka" Ltd. Company (Russia) and complied with the technical specifications 2245-001–14660125-07. The structure of the film included the following layers: high-density polyethylene, adhesive, co-polymer of ethylene and vinyl alcohol (EVOH), adhesive, and high-density polyethylene. The thickness of the layers was 16.5, 7.0, 18.0, 7.0, and 16.5 μm, respectively. The breaking strength of the polymeric material was 28–32 MPa.

As the components of a gas-modified medium, used for the packaging of samples, we used carbon dioxide and nitrogen in three different volumetric ratios; the first and third variants represented the maximum and minimum CO_2 content, respectively. The use of carbon dioxide as one of the medium components is caused by its high water solubility and inhibitory action on the aerobic microflora, including pathogenic microorganisms. Nitrogen is an inert gas and is characterized by a low water and oil solubility; it is used to prevent the oil oxidation and to displace the rest of oxygen from the packaging.

The samples, packaged without the use of a gas medium and vacuum, were used as the control.

The chilled salmon was stored at +4 ± 0.5º C ($P > 0.95$).

According to the planned program, we took first samples for our study after a 24-h storage, and then at the 7^{th}, 10^{th}, and 14^{th} days. We examined some organoleptic parameters, such as the appearance, color, and consistence, the smell on the surface and inside the product, the smell of the vapor, broth, and boiled product, and the taste of the boiled product, on their compliance to the State Standard 7631–2008. The microbiological parameters (quantity of mesophilic aerobic and optional-anaerobic microorganisms (QMA&OAMO), bacteria from the colibacillus group, *Staphylococcus aureus*, *Salmonella*, *Listeria monocytogenes*, and *Vibrio parahaemolyticus*, regulated by the Sanitary Standard 2.3.2.1078-01), were studied using the common methods.

Since the heightened CO_2 content in a gas medium can stimulate the growth of lactobacteria (Dubrovskaya, 2000), we additionally determined the total amount of lactobacteria according to the State Standard 10444.11–89.

The protein and non-protein nitrogen content were determined using a Kjeltek-2300 analyzer (Foos company). To determine the lipid content, we used the Bligh and Dyer method (Bligh and Dyer, 1959). The oil acidity index was determined according to the State Standard 7636–85.

The result of the organoleptic analysis showed that, during the whole period of the examination, the appearance, color, and consistence of the samples did not change and corresponded to this sort of product. At the 7^{th} (control) and 10^{th} (variant 1) days we registered a foreign smell on the surface and inside the product and in the vapor and broth during the boiling of the fish.

The organoleptic properties of the samples of the variants 2 and 3 (smell inside and on the surface of the product, smell of the vapor and broth, color and transparency of the broth, smell and taste of the boiled fish) corresponded to this sort of product up to 14^{th} day of the storage.

The results of microbiological studies showed the absence of the following microorganisms during the whole experimental period: colibacillus group (in 0.01 and 0.001 g of the product), *Staphylococcus aureus* (in 0.1 and 0.01 g), *Salmonella* (in 25 and 50 g), *Listeria monocytogenes* (in 25 and 50 g), and *Vibrio parahaemolyticus* (in 1.0 g of the product).

In the beginning of the storage, the QMA&OAMO value did not exceed the normalized value and varied from $7.4x10^3$ to $1.3x10^4$ CFU/g (Table 1). In the case of the control samples and samples from the variant 1, on the 7^{th} day we observed the exceeding of the above-mentioned value ($9.6x10^5$ and $7.5x10^5$, respectively). On the 10^{th} and 14^{th} days the samples from the variants 2 and 3 corresponded to the requirements of a normative documentation.

Table 1. Total microbe contamination of the chilled salmon samples during the storage, CFU/g

Variant	Sanitary requirements (SanPiN 2.3.2.1078-01)	Storage period, days			
		Background	7	10	14
1	No more than $1.0x10^5$	$7.4x10^3$	$7.5x10^5$	$3.2x10^5$	$9.9x10^4$
2		$5.3x10^3$	$6.4x10^4$	$5.9x10^4$	$4.0x10^4$
3		$1.3x10^4$	$8.7x10^4$	$7.7x10^4$	$2.8x10^4$
Control		$3.2x10^3$	$9.6x10^5$	$1.2x10^6$	$2.5x10^6$

The obtained results showed that the total quantity of lactobacteria in the samples of the variant 1 (the maximum volume fraction of CO_2) varied from $2.5x10^3$ (1^{st} day) to $8.5x10^4$ CFU/g (14^{th} day). In the case of the variants 2 and 3, where the volume fraction of CO_2 was minimal, the value of this parameter did not exceed $3.2x10^3$ CFU/g during the whole storage period. The maximum CO_2 amount within the packaging stimulates the growth of lactobacteria that corresponds to the data of other authors.

The total protein content in the examined samples varied from 18.1 to 20.5%.

To the end of the first 24 h, the non-protein nitrogen content in the fish products was 1.8–2.0% of the total nitrogen content. During the storage period, we observed a triple increase in the non-protein nitrogen content in the control samples and the samples of the variant 3 (6.1% of the total nitrogen content), whereas in the case of the variants 1 and 2 the value of this parameter increased in 2.0–2.5 times (3.8 and 4.7% of the total nitrogen content).

The lipid content in the chilled salmon samples varied from 20.2 to 26.5%.

The background level of the oil acidity index was 1.1–1.3 mg of KOH/g (Table 2).

The most intensive process of the accumulation of pyrolysis products, or free fatty acids, was observed in the control samples and the samples of the variant 1, where the acidity index exceeded the background value in 2.0–2.5 times to the 14^{th} day of storage. An increase in this index to the 14^{th} day in the samples of the variants 2 and 3 was significantly lower, comparing to the control samples and samples of the variant 1.

Table 2. Acid values of chilled salmon samples, packed in a gas mixture, mg KOH per 1 g of oil

Variant	Storage period, days			
	background	7	10	14
1	1.2	1.9	2.0	2.3
2	1.3	1.4	1.6	1.8
3	1.1	1.4	1.5	1.7
Control	1.21	1.6	2.1	3.11

The obtained results confirmed the reduction of the intensity of hydrolytic processes in proteins and lipids.

Thus, the result of our study made it possible to conclude that the polymeric materials with barrier properties can be used to provide the quality and safety of the chilled salmon production in the gas medium with the maximum volume fraction of nitrogen and minimal volume fraction of CO_2 at the storage temperature equal to 4^0C.

WHITE SEA MUSSELS *MYTILUS EDULIS* L. AS A SOURCE OF N-3 POLYENIC FATTY ACIDS

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The blue mussels, *Mytilus edulis* L. (1758), cultivated on artificial substrates in experimental aquaculture in the Kandalaksha Bay, White Sea, are, like most marine organisms, rich in polyunsaturated fatty acids (PUFA) of the linolenic (n-3) family, originating from phytoplankton. Uptake of various n-3 PUFA with food is known to reduce the risk of cardiac ischemia in humans. Furthermore, the groups of people whose diet is rich in these acids have lower blood coagulability, which is attributed to lower platelet aggregation, blood pressure reduction, weakening of triglyceride and cholesterol circulation (Sergeeva and Varfolomeeva, 2006). PUFA of the n-3 family were found to benefit patients with arthritis, kidney disorders, as well as other inflammatory and immune diseases (Lands, 1992; Mevkh et al., 1996; Bernardi, 1996). At present, one distinguishes the effects of three main fatty acids of the n-3 family: linolenic (18:3), eicosapentaenoic (20:5) and docosahexaenoic (22:6) acids. Eicosapentaenoic acid is the source of products which counteract substances of the arachidonic cascade. Docosahexaenoic acid is essential for the central nervous system (Lauritzen et al., 2000; Jump, 2002).

Comparative analysis of the total lipid fatty acids composition in some species of bivalves from the White Sea, such as *Mytilus edulis* (aged 5–6 years, shell size 65.8 mm), *Hiatella arctica* (shell size 26.6×14.5×12.2 mm) and *Modiolus modiolus* (shell dimensions 63.7×32.7 mm), showed *Mytilus edulis* to contain higher concentrations of both n-3 PUFA and total PUFA (Tab. 1). The proportion of arachidonic 20:4 (n-6) acid was the same in all three species.

Table 1. Fatty acid composition of some bivalves from the White Sea (% of total fatty acids)

Fatty acids (% of total FA)	*Mytilus edulis*	*Modiolus modiolus*	*Hiatella arctica*
Total saturated FA	17.9	22.8	22.8
Total monounsaturated FA	22.1	27.0	24.4
16:4(n-3)	4.6	1.4	1.0
18:3(n-3)	2.1	1.7	1.2
20:5(n-3)	15.4	17.3	10.9
22:6(n-3)	19.4	9.9	16.8
Total n-3 PUFA	44.4	35.8	35.9
20:4(n-6)	2.7	2.7	2.7
Total n-6 PUFA	11.6	10.0	9.6
Total PUFA	60.1	48.3	51.5

Detailed study of the fatty acid composition in cultured *Mytilus edulis* L. mussels from the White Sea showed the content of n-3 PUFA to increase with age (owing to 18:3 (n-3), 20:5 (n-3), 22:6 (n-3) acids), and peak at an age of 4–6 years (Tab. 2).

Interestingly, the content of n-6 PUFA, including the main representative of the series – arachidonic 20:4 (n-6) acid, was about the same, irrespective of the mussels' age (Tab. 2).