INVESTIGATIONS MICRORELIEF OF THE SURFACE, DIELECTRIC PROPERTIES AND FLUORESCENCE SPECTRUM OF NATURAL COMPOSITE - FISH SCALES

Gojayev E.M.[1], Nabiyev N.S.[2]. Ramazanov M.A.[2], Kahramanov K.Sh.[1]. Alieva Sh.V.[1], Ismailov A.A[1].
1 Azerbaijan Technical University, etc. Javid 25, Baku, AZ1073, Azerbaijan.
2 Baku State University
E-mail: geldar-04@mail.ru

ABSTRACT

In this paper, for creating highly sensitive and high-speed devices identified a new type of composite materials-fish scales, which are natural polymers. Fish scales are mineralized layer plates between which are collagen fibers. By the methods of atomic - force microscope (AFM) were investigated surface microrelief in 2D and 3D scale. The frequency dependence of the dielectric constant, dielectric loss, surface density of space charges of natural composite - fish scales of Kutum studied in the frequency range 0 -10^3kHz. Discovered that the main mechanoreceptor units of the lateral line is neyromasty, this contains several sensitive hair cells. These hair cells are similar to the sensory cells of hearing on the receptor cells neyromasty end in the branching efferent nerve fibers. Irritants receptors are streams of water and low-frequency oscillations of the medium. It was also revealed that, in a narrow frequency range 0-1kHz reduced and in a wide range 1-1000 kHz remains constant. Right and left side fish scales have the same dielectric characteristics.

Using a spectrofluorimeter Cary Eclipse fluorescence spectrum studied the fish scale in a wavelength 200-600nm. It was revealed that, the excitation signal wavelength 396.96, 388, 265.93 and 253.64 of the fluorescence observed at a wavelength of 541.02, 528.96, 362.00, 495.97, respectively, and the intensity of the detected fluorescence peaks almost all comparable intensity of the exciting signal Kutum fish has fluorescent properties and can be successfully used in technology.

Key words: Kutum fish, fish scales, surface microrelief, dielectric properties, the fluorescence spectrum

INTRODUCTION

In recent years, many scientific and practical significance of the study is to obtain new formulations of composites based on organic polymers with solid additions, the study of surface topography by atomic force microscopy and dielectric properties of the compositions. Addition of inorganic nature fillers in a polymer matrix is a universal method of modifying polymers. In particular, for extending the scope of their application in high density polyethylene (HDPE) and low density polyethylene (LDPE) were first introduced as fillers ternary compound semiconductor type (where A is Tl, B - In, Ga, C - S, Se) and their solid solutions basis. These studies showed that, the lifetime data composites 50 - 500 times longer than the lifetime of pure polyethylene and they are valuable materials [1-3]. In [4] presents the results of studies of the fluorescence spectra of composite materials of PE + x vol. % $TlGaSe_2$ (x = 0, 1, 5, 10, 20) in the wavelength range 400-600 nm. The effect of fluorescence found and between the composition of the composite and the fluorescence spectrum there is a qualitative relationship, depending on the wavelength. Investigated the temperature dependence of dielectric constant and dielectric loss tangent composites HDPE + x vol. % $TlGaSe_2$ (x = 0, 1, 3, 5, 7, 10) in the temperature range 300-500 K. It is shown that, the effects seen in the fluorescence spectrum of composite materials x=0÷ 20% $TlGaSe_2$ are similar, except for the composite PE+5 %$TlGaSe_2$ and the intensity detected at different wavelengths can be controlled by the amount of filler $TlGaSe_2$.

In papers [5-6] using the fluorescence spectrum were determined biologically active substances in organized media. In [7] were conducted studies of the effect of chlorophyll fluorescence of plants and developed the theoretical method for determining indicators of ecological stress.

Nanocomposites which occur in the living world are also attracted large scientific - practical interest. In the living world are countless types of composites, this timber plants and animal bones and tissue function of all organisms. These natural matrix nanocomposites are mainly organic polymers. One

of the most common bionanocomposites are the materials of which are made up of scales and fins of fish. Therefore, in recent years much attention is paid to their study. This is because fish skin covered with scales; the presence not paired fins (fish interfere with rotation around its axis, is carried forward movement), and paired fins -provides maintaining balance and turns; lateral line -provides sensitivity direction and rate of water flow. Besides fish skin protects the body from harmful environmental influences involved in metabolism. Through it are isolated and absorbed salt, oxygen, water and other substances. On the skin are nerve endings, so it can perform the function of sensory organs. The surface of the outer layer of porous flakes has various sizes depending on the location. In [8-9] spent researches have shown that, fish scales are mineralized layer plates, between which there are collagen fibers that are natural polymers. When the processes of formation of polymer flakes of fish guasifractal possibility approach to the processes of formation of their structures. It is shown that, the sparse surface of fish scales is guasifractal biopolymer structure and performs the functions of sensory systems. According to [10-12] fish scales composed of natural polymers - collagen. Collagen - natural polymer belonging to the group scleroproteins. Primary structure of the collagen polypeptide chain is composed of alternating residues of aminoacids. Dislike other proteins in the collagen predominate hydroxyproline, proline and glycine, hydroxyproline and collagen is a specific mark, as it contains no more than for any other protein. As you know: fish scales are collagen raw material - source of ihtiojelatin. Application areas of gelatin varied. It is widely used as a structurant in the food industry, is included in the food composition of films, coatings, edible casings used during cultivation of the microorganisms, and also used in medical and photographic industries. In some cases it ihtiojelatin used as adhesives. Ihtiojelatin structurant is natural, so the restrictions in its application no. The use of scales as a secondary resource is limited due to the nature of the structure and chemical composition of different scales of other collagen-containing fish waste. Currently processing scales is to fish combines a serious problem. The results of the research have developed a technology for producing ihtiojelatin from scale. Due to changes in the resource base became necessary to develop the technology of ihtiojelatina Scale ordinary fish and pond fish species, commodity stocks are significant. In order to develop a rational, science-based, waste-free efficient processing technology scales, have been studied the chemical composition and the specific properties of the raw material. There are three types of scales: placoid (sharks, skates and rays), ganoid (sturgeon), cycloid, and ctenoid (bony fish). Teleost fish scales consist of two layers: a solid top (gialodentin), strongly mineralized layer formed of thin bony plates cemented with organic matter, 60-70% represented about that collagen. Weight scales in different species varies in the range 2,4-9,7% by weight. Scales of bony fish has the form of thin solid circular plates, so the characteristic dimension was taken diameter. Depending on the type of fish scales can be different sizes from 5 -23 mm. The most powerful scales in carp and crucian carp, bream then, the smallest pike, pike-perch and carp. One of the specific features of a scale adhesion of scales in the pre-preparation and extraction of raw materials, so it is suitable to intensify the hydrodynamic performance of the mass transfer process, some of the known methods, given the lability of the raw material to a certain stress. The study of the chemical composition of certain types of ordinary fish scales and pond fish showed the presence of scales, depending on the type of fish 39-62% of nitrogenous substances; 28,5-49,5% minerals and negligible fat content - less than 0.2%. According to the authors [13] the size, shape and structural features of the scales are important determinant of future operations of technological process of ihtiojelatin, since an increase in the contact surface ensures a high rate of diffusion during the mass-transfer processes. However, for the use of scales in the solution of other problems, a study of the microrelief of the surface and the fundamental physical characteristics.

The purpose of this work - study of surface microrelief, dielectric properties and fluorescence spectra of fish scales.

EXPERIMENTAL TECHNIQUE

Investigation the surface microrelief of fish scales were carried by atomic - force microscope. For study, the scales were taken from the side of the fish Kutum. Investigation of surface microrelief and its local properties is carried out using a special way prepared probe in the form of needles. Working part probes has dimensions of about 10 nm. Typical distance between probe and sample surface in probe microscopes is the order of magnitude 0.1-10 nm. At the heart of the probe microscopes are different types of interaction between the probe and the surface. Probe moves along the first in the direct and then in the reverse direction, then moves to the next line. Motion of the probe is carried out using a scanner in small steps under the influence of sawtooth voltage generated by digital-to-analog converters. Registration information about surface is made, as a rule, on a direct passage to the following two conditions: during scanning probe touched all points of the surface, and at every moment of the probe touched the surface of only one point. To determine the dielectric permittivity ε of fish scales (Kutum) measured capacitance (C) of the sample. Permittivity of the material is calculated from the measured capacitance, the thickness of the sample and the electrode area. Permittivity (ε) is calculated by the formula:

$$\varepsilon = \frac{Cd}{\varepsilon_0 S},$$

where, C is the measured electrical capacitance of the sample, F; ε_0 = 8,85 10^{-12}F/m; d- thickness of the sample, m; S - area of the sample. Dissipation factor is measured directly. Thus, for each of the selected samples measured capacitance and dielectric loss tangent corresponding to the frequencies - 1 kHz. The sample was mounted between two electrodes in the measuring cell. Then the sample was heated in a chamber using a heater which mounted in the cover with a constant speed of 2K/min. The sample temperature was recorded by using a thermocouple, a temperature meter, and dielectric loss and dielectric constant at a measuring bridge E7-8. Heating with a constant velocity is achieved using three-LATR-system. Research luminescent properties of fish scales were performed using spectrofluorimeter Cary Eclipse. The device is versatile for studying the spectral properties of samples of different nature. The device is focused on the use of biological and materials science applications. The excitation source is a pulsed xenon lamp, with specification-80 flashes per second, 75 kW equivalent powers under the peak. Focusing optics is Schwarzschild collector. Using the construction Czerny - Turner monochromator and controlled horizontal slot. There are six selectable slits: 1.5, 2.5, 5, 10, 20, 10mm. Eclipse includes a monochromator and 2 can be carried out independent of each scanning monochromator. If fixed excitation monochromator scanning emission monochromator obtained emission spectrum or often called the fluorescence spectrum. The emission spectrum is information about the molecular structure and the nature of the material. Form fluorescence spectrum does not depend on the wavelength of the excitation light, since the emission is generated by the lowest of the excited states. The fluorescence spectrum is often a "mirror image" of the absorption spectrum. Fixing emission monochromator and scanning monochromator excitation can be obtained fluorescence excitation spectrum. Excitation spectrum is the dependence of the emission intensity at a given wavelength by scanning the wavelength of the exciting light. Can be carried out simultaneously scanning both monochromators and obtain spectra of synchronous scanning.

EXPERIMENTAL RESULTS AND DISCUSSION

We have conducted studies of the surfaces of fish scales showed that sensitive receptor cells of the lateral line may form isolated clusters in the skin, but more often they are found at intervals in the grooves of the body. Channels can be completely closed depressions in the skin. Part of the receptors of the lateral line are converted into electroreceptors and can detect electric vibrations of the environment (Figure.1,2). Each dashed line represents a lateral canal or furrow filled with mucus, which can be facilitated and the fractal nature of the porous morphology of the lateral line. Cells of the lateral line are collected in kidney-

shaped groups and hidden in the channels, which are washed with water. Major role in the dynamics of movement play nanostructures on the surface of scales and fins. Scales Kutum riddled with holes leading into the skin (Figure 1, 2). Beneath them runs a channel that extends to the head and branches there around the eyes and mouth opening. Branched channels on the head and bones are inside and have to go outside. In the presented fragments AFM -Images visible lateral line organs (Figure 2) extending along the outer surface of the scales, they are: the hole in the lateral line scales, the lateral longitudinal channel line-sensitive cells, nerves. Scales of the lateral line canals filled with a liquid containing a specific ion composition. In the channel walls as noted tested nerves that carry signals from the environment. The main mechanoreceptor units of the lateral line are neyromasty, each of which contains a number of sensory hair cells. These hair cells are similar to the sensory cells of hearing. On the receptor cells neyromasty end branching efferent nerve fibers. Irritant receptors are streams of water and low-frequency oscillations of the medium. Dependence of the dielectric constant and dielectric loss versus frequency for two symmetrical scales of fish (Kutum) is shown in Figure 3. Studies were conducted in the frequency range 0-1000kHz. As follows from Figure 3 at low (0.01 - 1 kHz) frequencies, a significant decrease of the dielectric constant from 34.72 to 10.97. In the frequency range 1-20 kHz revealed a minimum at the frequency of 9.6 kHz and a maximum at the frequency of 10 kHz, and later, with a change in frequency to 10^3 kHz - ε remains constant. A similar variation of the dielectric constant depending on the frequency detected and second scales. Minimum is observed at a frequency of 2.8 kHz and maximum at a frequency 5,1 kHz. Such a behavior of the function ε (ν) indicates the nature of the relaxation dispersion of the dielectric constant [14, 15]. As relaxators can perform structural elements scales with different degrees of mobility, as well as a number of as yet unknown low molecular weight impurities. Characteristic of the test scales, the initial decrease in the dielectric constant and dielectric loss. It is known that at low frequencies, internal electric fields are distributed accordingly conductivity and high frequencies - respectively the dielectric constant. Consequently decrease ε with increasing frequency of the measuring field can be explained by the appearance of a relatively strong internal field in the scales of fish. Dependence of the dielectric loss of scales was also investigated in the frequency range 0 - 1000 kHz. As follows from Figure 4 at low frequencies for both scales is a strong decrease. However, one of the scales at 10 kHz dispersion is observed. In the future, with increasing frequency up to 500 kHz occurs moderate decrease in the dielectric loss. Starting with frequency 500 kHz observed a slight decrease in the dielectric loss. Decrease with increasing frequency as evidenced by the fact that at low frequencies, the main types of dielectric losses are losses in the electrical conductivity. Observed in high frequency domain dependencies ε (ν) and tgδ (ν) dispersion, determined apparently relaxation losses typical for most dielectrics. Results of the study of the surface charge density as well investigated in the frequency range 0-10^3 kHz. Results of the study are shown in Figure 5. As follows from Figure 5 at the frequency range 0-8 kHz surface charge density remains practically unchanged, and in the frequency range of 8 - 500 kHz is relatively strong, and in the range of 500 - 1000 kHz very strong increase. The emission spectrum wears information about the molecular structure and the nature of the material. The shape of the fluorescence spectrum does not depend on the wavelength of the excitation light, since the emission is generated by the lowest of the excited states. The fluorescence spectrum is often a "mirror reflection" of the absorption spectrum. Fixing the emission monochromator and scanning monochromator excitation can be obtained by fluorescence excitation spectrum. Excitation spectrum is the dependence of the emission intensity at a given wavelength by scanning wavelength of the exciting light. Can be carried out and simultaneous scanning of both monochromators and obtain spectra of synchronous scanning. A characteristic property of the fluorescence spectrum (SF) is a high resolution, accompanied by processes related to the chemical composition of the sample, the elements of the structure and other dynamic changes. SF has a fairly short range of time, as through 10^{-8} s after light absorption begins fluorescence. After this time, all processes take place at the molecular level. Nonradioactive energy transfer and the exchange of charges and energies between the components is reflected in the fluorescence spectra, in results of short-term dynamic processes in the study of static properties and structure properties, as well

as processes that are identified with light signal detected by narrow luminescence bands. Results of the study of the excitation spectra of fish scales are shown in Figure 6 the obtained spectrum reflects the characteristic radiation, which results from the excitation light flakes of fish length 230 nm. The spectrum includes various peaks, some of them correspond to the fluorescence and the charge of the fish scales in Figure 7. As seen from Figure 7 at signal excitation wavelength of 396.96, 388, 265.93 and 253.64 of the fluorescence observed at a wavelength of 541.02, 528.96, 362.00, and 495.97, respectively. The intensity of the fluorescence peaks identified in almost all comparable intensity of the exciting signal. So in the excitation wavelength of the fluorescence intensity of the peaks 396,96nm matter 28 a.u. (a.u. - the atomic unit of energy) and in the excitation wavelength of 380nm peak intensity of the fluorescence increases by 40a.u. Accordingly, the wavelength 265,95nm peak fluorescence intensity increases by 63a.u., when the excitation wavelength 253,64nm fluorescence intensity peaks is 13 a.u. Change in intensity on the one hand due to the uneven distribution of intensity in the spectrum of a xenon lamp, on the other hand to the difference in the quantum yield of fluorescence. Comparing the intensity of the excitation signal with the observed peak intensities of fluorescence can come to conclusions about what researched material has strong fluorescence properties. So, study the spectra of fluorescence fish flakes Kutum in the wavelength range 200-600nm, and found that these materials can be widely used in the multi-function electronic devices and used as a new type of composites with unique properties. Note that the effects observed in the fluorescence spectrum of the fish flakes Kutum can be controlled with the election of scales from different parts of the skin of fish.

CONCLUSION

Studied the state of the surface microrelief, the frequency dependence of the dielectric loss and the surface charge density of fish scales - Kutum by atomic force microscope. Revealed that, at low frequencies the dielectric constant and dielectric loss is greatly reduced, and at medium and low frequencies remain constant. The surface charge density on the contrary, at low frequencies remains constant, but at high frequencies is greatly increased. Revealed that, the fish scales of Kutum has fluorescent properties, can be used in multi-functional devices.

REFERENCES

1. G.A.Mamedov, EM Gojayev, AM Maharramov Sh.A.Zeynalov, Studies of surface topography by atomic force and dielectric properties of high density polyethylene compositions and additives $TlGaSe_2$ Electronic Materials Processing, 2011, 47 (6), 94-98.

2. E.M.Godzhaev, S.S.Safarova, D.M. Kafarova. K.D.Gyulmamedov, H. R. Akhmedov study surface microrelief and dielectric properties of the compositions of PP + TlIn0, 98Ce0, $02Se_2$ Electronic Materials Processing, Chisinau. 2013, 49 (4), 1-5.

3. E.M. Gojayev, A.M. Magerramov, Sh.A. Zeynalov, S.S. Osmanova, E.A. Allahyarov, Crown electrets based on high density polyethylene composites with semiconductor filler Academy of Sciences of the Republic Moldova. Kishinev. Electronic materials processing number 6, (266), 2010.

4. E.M.Godjaev, N.S.Nabiev, Sh.A.Zeynalov, S.S.Osmanova, E.A.Allahyarov, A.G.Gasanova, Studies of the fluorescence spectra and dielectric properties of composites of HDPE + x.% $TlGaSe_2$ Electronic materials Processing, 2013, 49 (3) -1814.

5. V.S. Lysenko, T.V. Vardun, V.G. Sawyer, V.P. Krasnov The fluorescence of chlorophyll in plant as an indicator of ecological stress: the method basis of theoretical // Fundamental research. 2013. № 4. pp 112-121

6. N.V.Nevryueva Determination of some biologically active substances, based on the effect of sensitized fluorescence in organized media. The abstract of dissertation for scientific degree of Candidate of Chemical Sciences, Saratov State University, 2008, 20 pp.

7. S.N. Shtykov, Kalashnikov N.V. T.D. Smirnov, Y.G. Konyukhova The Complexes with energy transfer in the excited state in organized media for fluorimetric determination of biologically active substances // Biomed. tehnol. and electronics. 2006. № 12. pp. 4-9.

8. E.M. Godzhaev, K.S. Kahramanov, Sh.V.Alieva, A.B. Naghiyev Guasifractal surface of fish scales, Education News. Applied chemistry and biotechnology, 2014, № 1, (6), p.56-61.

9.Eldar Godzhaev, Abbasali Abasov, Sharafkxanim Aliyeva, David Charuxcev // The Surface Fractal Structure of Fish Scales / / Open Journal of Inorganic Non-Metallic Materials, 2014, 4, 7-11.

10. O.S.Yakubova, A.L. Kitten / / Journal; Bulletin of Astrakhan State Technical University, 2 Production technology household cleaning products as a source of scales ihtiozhelatina 2004 Vol.2, pp.130 - 135.

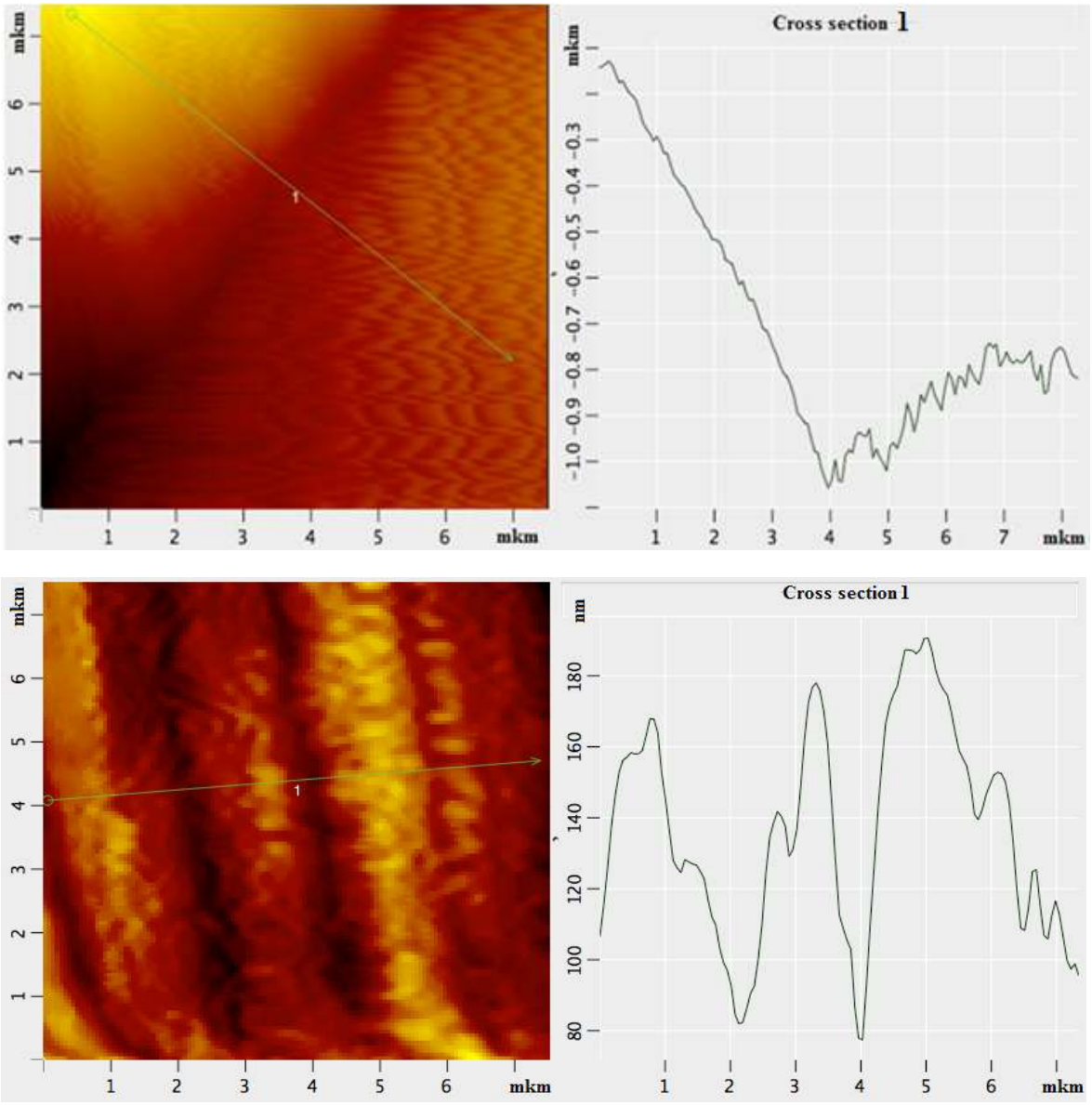
11. B.A. Bahgat. The fractal structure and the evolutionary process of the living. Journal of General Biology, Vol. 67, 2006. № 4, pp.243 -255.

12 B. Mandelbrot Fractal Geometry of Nature. - M .: Institute of Computer Science, 2002 - 656 p.

13. M. C. Gomez-Guillen, J. Turnay, M. D. Fernandez-Diaz, N. Ulmo, M. A. Lizarbe, P. Montero Structural and physical properties of gelatin extracted from different marine species: a comparative study // Food Hydrocolloids. - 2002. Vol. 54, № 1.- pp.25-34.

14. V.E. Mouradian., E.A Sokolov, S.D. Babenko, A.P. Moravian Dielectric properties of composites modified by carbon nanostructures in the microwave range. Technical Physics, 2010, 80 (2), pp.83-87.

15. M.M. Guliyev, R.S. Ismailov Electrical properties of composites filled with dispersed oxides. Electronic processing of materials. 2009 №4 pp. 48-51.



a) b)

Figure 1 Longitudinal section of the AFM images in 2D-scale surface of scales Kutum: the pore sizes fluctuate within ≈ 80nm, the maximum height of structures within ≈ 100 nm

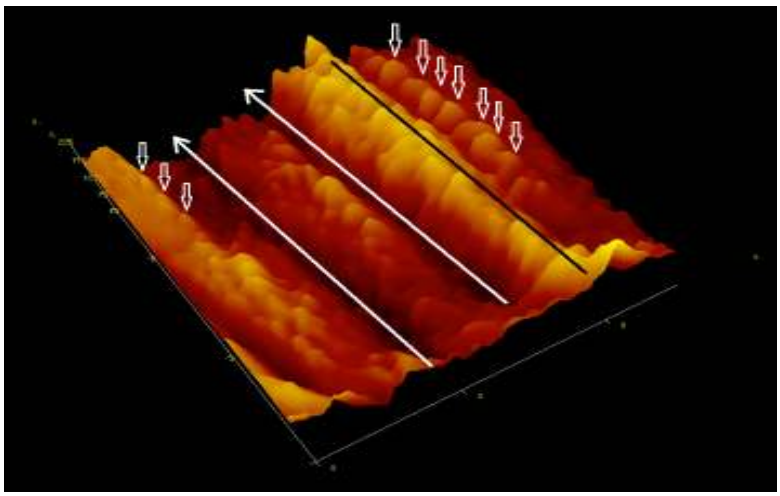


Figure 2 Fragment AFM images in 3D-scale surface of scales Kutum: longitudinal channels (marked with white lines) carried communication from head to tail. Individual nanoislands marked by vertical arrows. Black lines are marked coalesced nanoformulations -microclusters Scan: 7 x 7mkm

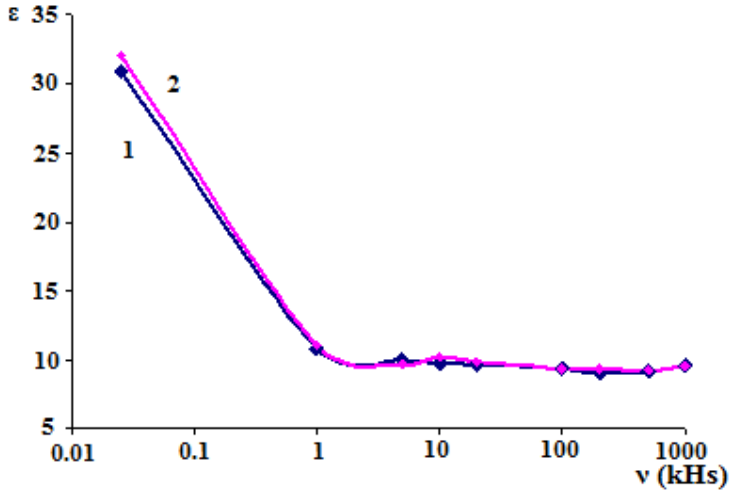


Figure 3 Dependence of the permittivity versus frequency for two scales of fish (Kutum) 1-left, 2- right side portion

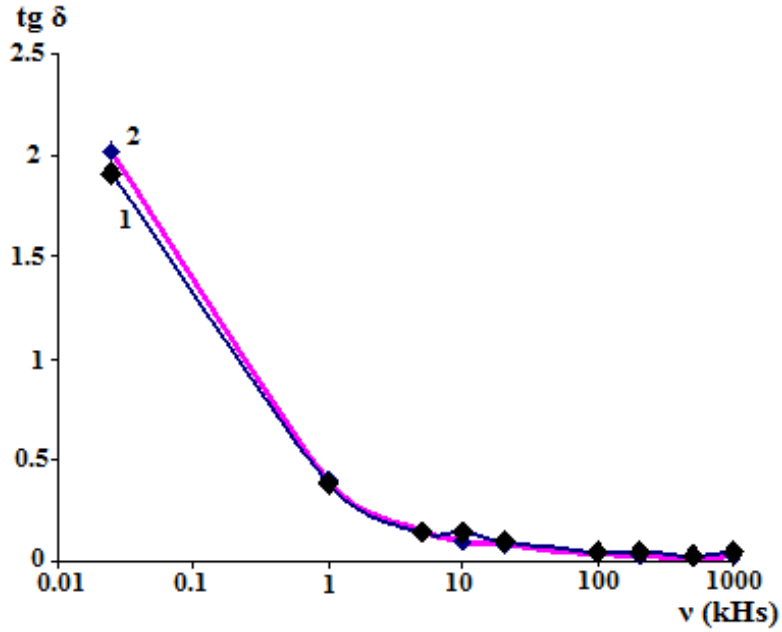


Figure 4 Dependence of the dielectric loss versus frequency for the two scales of fish (Kutum) 1-left, 2- right side portion.

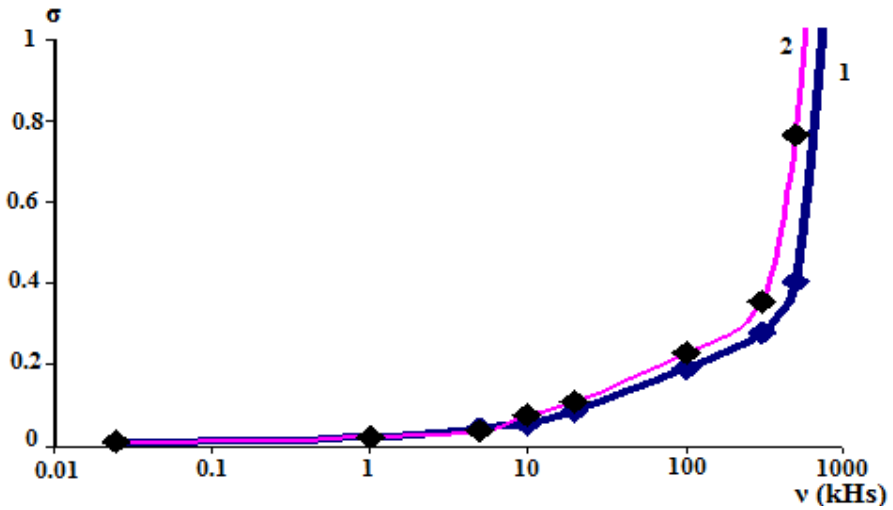


Figure 5 Surface charge density dependence with respect to frequency for two scales of fish (Kutum). 1-left, 2- right side portion.

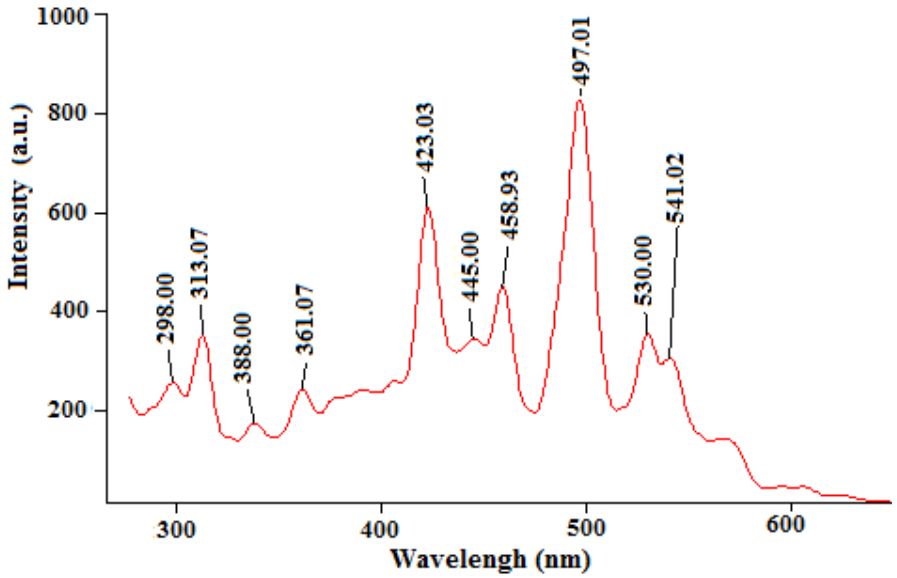


Figure 6. General excitation spectrum of fish scales.

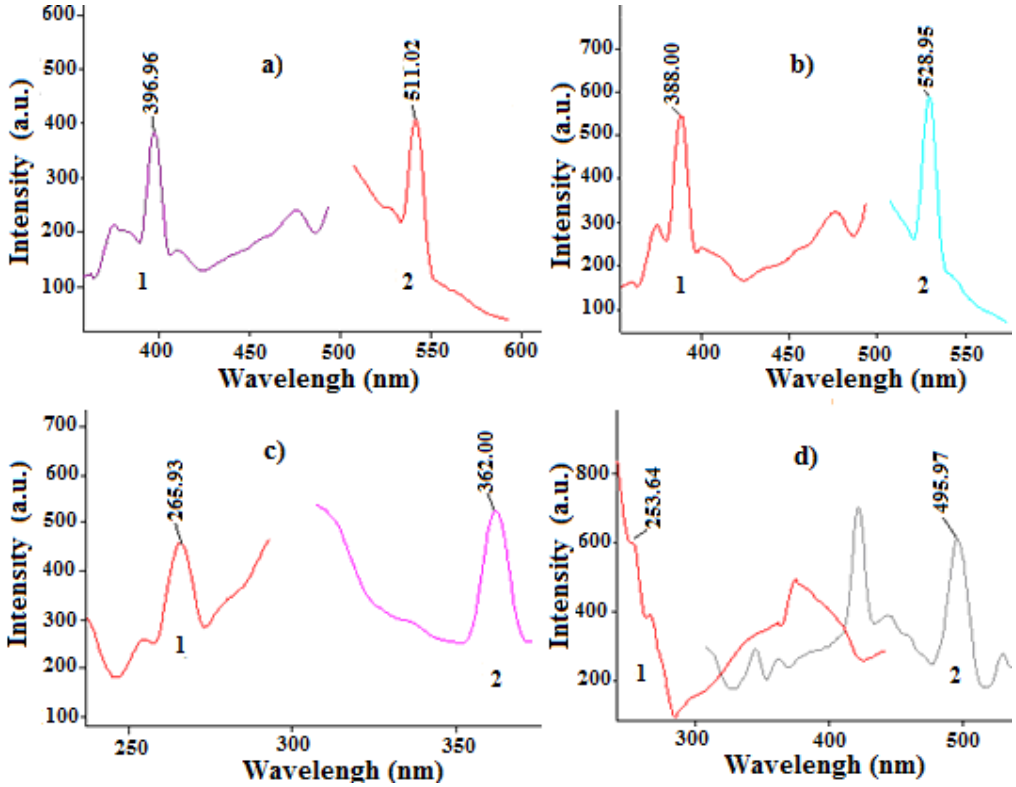


Figure 7 The fluorescence spectrum of fish scales at various excitations: 396.96 nm - 541.02 nm (a); 388 nm – 528.96 (b); 265.93 nm - 362.00 (c); 253.64 – 495.97nm (d) observed effects of fluorescence.