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

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In the paper presents the results of studies of surface microrelief by atomic - force microscope, the frequency dependence of the dielectric permittivity, dielectric loss, surface charge density and the fluorescence spectra of Kutum fish scales - matrix, which is a natural composite - collagen. Revealed that fish scales have efficient fluorescent properties and can successfully used in technique.

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

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13 INTRODUCTION

14 In recent years many scientific and practical importance has research aimed at getting new 15 compositions of composites based on organic polymers with semiconductor additions, the study of 16 surface topography 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, 17 for extending the scope of their application in HDPE (HDPE) and low density polyethylene (LDPE) were 18 19 first introduced as fillers ternary compound semiconductor type (where A is Tl, B - In, Ga, C - S, Se) and 20 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 21 22 studies of the fluorescence spectra of composite materials of PE + x, vol% TlGaSe₂ (x = 0, 1, 5, 10, 20) in the wavelength range 400-600 nm. The effect of fluorescence found and between the composition of the 23 24 composite, and the fluorescence spectrum there is a qualitative relationship, depending on the wavelength. The temperature dependence of dielectric constant and dielectric loss tangent composites 25 26 HDPE + x vol.% TlGaSe₂ (x = 0, 1, 3, 5, 7, 10) in the temperature range 300-500 K. It is shown that the 27 effects observed in the fluorescence spectrum in composites x = 0 on 20.% TlGaSe₂ similar except five of 28 the composite PE.% TlGaSe₂, and the intensity detected at different wavelengths can be controlled by the amount of filler TlGaSe₂. 29

30 Nanocomposites are found in the living world are also attracted great scientific and practical interest. In the living world are countless types of composites, this is a timber plants and animal bones, 31 and functional fabrics of all organisms. These natural matrix nanocomposites are mainly organic 32 33 polymers. One of the most common organic nanocomposites is a materials composed of scales and fins of fish. Hence, recently, much attention is paid research scales and fins of fish. This is because fish skin 34 35 covered with scales; presence of unpaired fins-(fish interfere with rotation around its axis, is carried forward movement), and paired fins, ensure the maintenance of equilibrium and turns; lateral line-36 37 direction provides the sensitivity and speed of the water flow. Besides fish skin protects the body from 38 harmful environmental influences, is 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 39 sensory organs. The surfaces of the outer layer of porous flakes have different sizes depending on the 40 41 location. According to [5-6] fish scales consists of natural polymers, collagen. Collagen - a natural polymer, belonging to the group of scleroproteins. Primary structure of the collagen polypeptide chain is 42 43 composed of alternating residues of amino acids. Unlike other proteins predominate hydroxyproline in 44 collagen, proline and glycine, hydroxyproline and collagen is a specific mark, as it does not contain more than in any other proteins. In [7-8] studies have shown that fish scales are mineralized layer plates, 45 46 between which there are collagen fibers that are natural polymers. When considering the processes of 47 formation of polymer flakes of fish possible quasi fractal approach to the processes of formation of their 48 structures. It is shown that sparse surface fish scales is a quasi fractal biopolymer structure and performs the functions of sensory systems. The aim of this work - study surface microrelief, dielectric properties 49 50 and fluorescence spectra of fish scales.

51 EXPERIMENTAL TECHNIQUE

52 Investigation of surface microrelief fish scales conducted by atomic - force microscope. To 53 investigate the scales were taken from the side of the fish Kutum. Investigation of surface microrelief and 54 its local properties is carried out using a special way prepared probe in the form of needles. Working part 55 probes has dimensions of about 10 nm. Typical distance between probe and sample surface in probe 56 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 57 in the reverse direction, then moves to the next line. Motion of the probe is carried out using a scanner in 58 small steps under the influence of sawtooth voltage generated by digital-to-analog converters. 59 60 Registration information about surface is made, as a rule, on a direct passage to the following two 61 conditions: during scanning probe touched all points of the surface, and at every moment of the probe 62 touched the surface of only one point. The dielectric permittivity ε fish scales (Kutum) measured 63 capacitance (C) of the sample. Permittivity of the material is calculated from the measured capacitance, 64 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; $\mathcal{E}_0 = 8,85 \ 10^{-12}$ F/m; d-diameter of the 66 67 sample, m; S - area of the sample. Dissipation factor is measured directly. Thus, for each of the selected dielectric capacitance to be measured and the dielectric loss tangent of the angle corresponding to the 68 69 frequencies - 1 kHz. The sample was mounted between two electrodes in the measuring cell. The sample 70 was then heated in a cell using a heater which is mounted in the cover with a constant speed of 2K/min. 71 The sample temperature was recorded by using a thermocouple and a temperature meter, and dielectric loss and dielectric constant at a measuring bridge LZHR E7-8. Heating with a constant velocity is 72 73 achieved using three-LATR-system. Research luminescent properties of fish scales were performed using 74 spectrofluorimeter Cary Eclipse. The device is versatile for studying the spectral properties of samples of 75 different nature. The device is focused on the use of biological and materials science applications. The 76 excitation source is a pulsed xenon lamp, with specification-80 flashes per second, 75 kW equivalent 77 powers under the peak. Focusing optics is Schwarzschild collector. Using the construction Czerny -78 Turner monochromator and controlled horizontal slot. There are six selectable slits: 1.5, 2.5, 5, 10, 20, 79 10mm. Eclipse includes a monochromator and 2 can be carried out independent of each scanning 80 monochromator. If fixed excitation monochromator scanning emission monochromator obtained emission spectrum or often called the fluorescence spectrum. The emission spectrum is information about the 81 82 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 83 84 fluorescence spectrum is often a "mirror image" of the absorption spectrum. Fixing emission 85 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 86 87 scanning the wavelength of the exciting light. Can be conducted simultaneously scan both 88 monochromators and obtain spectra of synchronous scanning.

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90 EXPERIMENTAL RESULTS AND DISCUSSION

Center studies the surface 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 fully enclosed depressions in the skin. Part of the lateral line receptors are converted into electro-receptors and can detect the electrical oscillations of the environment (Fig. 1, 2). Each dashed line represents the lateral channel or furrow filled with mucus, which can be facilitated and the fractal nature of the porous morphology of the lateral line. Cells were collected in the lateral line and a kidney groups hidden in the channels, which are washed with water. Major role in the dynamics of movement play

98 nanostructures on the surface of scales and fins. Scales Kutum riddled with holes leading into the skin 99 (Fig. 1, 2). Beneath them runs a channel that extends to the head and there is branches around the eves and mouth opening. Branched channels on the head and bones are inside and have to go outside. In 100 representation of the AFM images visible lateral line organs (Fig. 2) extending along the outer surface of 101 102 the scale is: holes in the lateral line scales, lateral longitudinal channel line-sensitive cells, nerves. Lateral 103 line scales containing channels filled with a liquid of specific ion composition. In the channel walls 104 extend as noted nerves that carry signals from the environment. The main mechanoreceptor units of the 105 lateral line are neuromasts, each of which contains several sensory hair cells. These hair cells are similar to the sensory cells of hearing. At the receptor cells of neuromast branching is efferent nerve fibers. 106 Irritant receptors are streams of water and low-frequency oscillations of the medium. Dependence of the 107 permittivity and dielectric loss versus frequency for the two scales of fish (Kutum) is given in Figure 3. 108 109 Studies were conducted in the frequency range 0-1000kHz. As Figure at very low (0.01 - 1 kHz) frequencies is a significant decrease of the permittivity of 34.72 - to 10.97. In the frequency range 20 110 kHz-1 revealed a deep minimum at a frequency of 9.6 Hz (9.61) and a maximum at a frequency of 10 111 112 kHz (10.1) and later, with a change in frequency to 103kGts - ε remains constant. A similar variation of 113 the dielectric permittivity depending of frequency detected on the second scale. Minimum is observed at a frequency of 2.8GHz and a maximum at a frequency of 5.1 kHz. Dependence of the dielectric loss of 114 scales was also investigated in the frequency range 0 - 1000 kHz. As follows from Figure 4 at low 115 frequencies for both scales is a strong decrease. However, one of the scales at a frequency of 10 kHz is 116 observed variance. In the future, with increasing frequency up to 500 kHz occurs moderate decrease of 117 the dielectric loss. Starting with the frequency of 500 kHz, been an increase the dielectric loss up to 1000 118 kHz. Results of the study of the surface charge density have been also investigated in the frequency range 119 120 0 - 103kGts. Results of the study are shown in Figure 5. As follows from the figure in the frequency range 0 - 10kHz surface charge density remains practically unchanged, and in the frequency range 10 - 500 kHz 121 is relatively strong, and in the range 500 - 1000kHz very strong increase. A characteristic property of the 122 123 fluorescence spectrum (SF) is a high resolution, accompanied by processes related to the chemical 124 composition of the sample, the elements of the structure and other dynamic changes. SF has a fairly short range of time, as in 10-8s after light absorption begins fluorescence. During this period all processes take 125 126 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 the short-term results of dynamic 127 processes in the study of static properties and properties, as well as processes that are identified with 128 129 using light signal detected narrow luminescence bands. Results of the study of fish scales excitation 130 spectra are shown in fig.6. The resulting spectrum reflects the characteristic radiation, which can be 131 obtained upon excitation with light fish flakes length 230 nm. The spectrum includes various peaks, some of which correspond to the fluorescence and fish scales in the charge of Fig. 7. As seen from Fig.7. At 132 signal excitation wavelength 396.96, 388, 265.93 and 253.64 effects observed fluorescence at 133 wavelengths of 541.02, 528.96, 362.00, and 495.97. Peak fluorescence intensity detected in virtually all 134 comparable intensity excited signals. So at excitation wavelength of 396.96 nm fluorescence intensity of 135 the peaks has a value of 28 AU (AU - the atomic unit of energy) and at excitation wavelength of 380nm 136 137 peak fluorescence intensity increases by 40a.e. Accordingly, the wavelength of 265.95 nm fluorescence intensity of the peaks increases by 63a.e. and at excitation wavelength of 253.64 nm fluorescence 138 139 intensity of the peaks at 13 AU Change in intensity on the one hand due to the uneven distribution of 140 intensity in the spectrum of a xenon lamp, on the other hand with the difference in fluorescence quantum yield. Comparing the intensity of excitation signals to the observed peak intensities of fluorescence can 141 142 come to conclusions about what researched material has strong fluorescence properties. Thus, the 143 fluorescence spectra of investigated fish flakes Kutum in the wavelength range 200-600nm, and found that these materials can be widely used in electronic devices and multifunctional used as a new type of 144 composites with unique properties. Note that the effects observed in the fluorescence spectrum in Kutum 145 146 fish flakes can be controlled elections scales from different parts of the skin of the fish.

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148 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. Revealed that fish scales Kutum has fluorescent properties, can be used in multi-functional devices.

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

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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 * 7mkm



scales of fish (Kutum)



REVIEW UNDER PEER



