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Surface Micro-Relief And Dielectric Properties Of LDPE + x vol.% fs and LDPE + x vol.% $Bi_{0.5}Sb_{1.5}Te_3$ Composites

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The paper describes the technology of obtaining and results of research of surface micro-relief of biocomposite LDPE + x vol.% FS (fish-scale) obtained on the base of low density polyethylene with fish scale fillers, and LDPE + x vol.% $Bi_{0.5}Si_{1.5}Te_3$ composites with the addition of $Bi_{0.5}Si_{1.5}Te_3$ semiconductor compound. Using atomic-force microscope in 2D and 3D modes surface and three-dimensional images of composites were obtained. The results of the study of the frequency dependence of the dielectric permittivity and dielectric loss for LDPE + x vol.% FS composites in the frequency range 25-1 MHz are presented. It was found that the dielectric permittivity with increasing of volume fraction of biological origin filler decreases over the entire frequency range.

INTRODUCTION

In recent years, big scientific-practical importance have researches, aimed at obtaining new composite structures based on organic polymers with various fillers.

Nanocomposites which are found in the living world are also attracted great scientific and practical interest. In the living world no end of types of composites, they are wood plant and animal bones, and functional tissues of all organisms. These matrix of this natural nanocomposites are mainly organic polymers. Some of the most common bio-nanocomposites are materials of which are made up fish scales. Therefore, in recent years great attention is paid to their study.

The flakes have different sizes depending on the location. Elsewhere [1] by studies have shown, that fish scales are mineralized layer plates, between which are located the collagen fibers that are natural polymers.

Collagen is natural polymer belonging to the scleroprotein group. The primary structure of the collagen is a polypeptide chain composed of alternating amino acid residues [2, 3, 4]. Unlike other proteins in collagen prevail hydroxyproline, proline and glycine, at that hydroxyproline is a specific mark of the collagen, as it does not contain in any other proteins. As is well known, fish scales are the collagen raw material - source of ichthyogelatine. Applications of the gelatin are diverse [5]. It is widely used as a structure-former in the food industry, and is a part of the plastic wraps, coatings, edible casings, used in the cultivation of microorganisms, and also used in the medical industry and photo-indusrty [6, 7, 8]. In some cases ichthyogelatine is used as glue matter. The scales of bony fish are composed of two layers: a solid top (hyalodentnum) strongly mineralized layer formed of thin bony plates, cemented by organic matter, for 60 ÷ 70 % represented by protocollagen. Weight scales in different species varies in the range 2.4 ÷ 9.7 % by weight [1]. The scales of bony fishes have the appearance of fine solid round plates, so a diameter was taken as the characteristic dimension. Depending on the type of the fish scales may be of different sizes from 5 ÷ 23 mm. The most powerful scales at common carp and crucian carp and then at bream, the smallest scale at pike, walleye and silver carp. One of the specific properties of the scales is adhesion of scales in the process of pre-treatment and the extraction of raw materials, so it is advisable to intensify the hydrodynamic performance of the mass transfer processes by some of the known methods, taking into account the liability of raw materials to certain influences. Investigation of the chemical composition of the scales for certain types of the ordinary fish and pond fish showed the presence in scales depending on the type of fish 39 ÷ 62% nitrogenous substances; 28.5 ÷ 49.5% mineral matters and a minor content of fats - less than 0.2%. According to the authors of [7], the size, shape and features of the structure of the scales are an important factor in determining the next steps of the process obtaining ichthyogelatin, since an increase in the contact surface provides high diffusion rate during the mass transfer processes. However, for the use of scales in solving other problems the study of micro-relief surface and basic physical characteristics is required.

The purpose of this work is the study of surface micro-relief and dielectric properties of bio-composites on the base of the low-density polyethylene with fish scales fillers.

Experimental Procedure

For preparing biocomposites as matrix low density polyethylene (LDPE) of mark M – 158, and as a filler - fish scales (FS) was used. For obtaining filler powders ar first fish scales were thoroughly purified and dried, with a gradual increase from room temperature to 50^{o}C, and held at this temperature for 10 minutes. Thus dried fish scales were ground in a special mill to a powder. Bio-fillers content in composites varied in the range of 5 to 15 vol.%. Composites prepared from the homogenous powder mixture of the filler and matrix components using heated press at a temperature of 420 K and a pressure of 15 MPa. Quenching crystallization mode - fast cooling the samples in the ice-water mixture. Samples for measurement of dispersion curves of dielectric characteristics were prepared in the form of discs of 50 mm in diameter and about 170 microns thick. A reliable electrical contact of the electrodes provided by lubrication a silver paste. Measuring the dielectric permittivity (ε) and dielectric loss ($tg\delta$) were implemented using E8-7 bridge on AC at a frequency range of 25 ÷ 1000 kHz as described elsewhere

[9]. Measurement error for ε and $tg\delta$ were 5 and 9%, respectively. The dielectric constant was calculated using the formula:

$$\varepsilon = \frac{Cd}{\varepsilon_0 S} \qquad (1)$$

where C is measured electrical capacitance of the sample, F; ε_0 = 8.85·10^{-12} F/m - the dielectric constant; d - diameter of the sample, m; S - area of the sample.

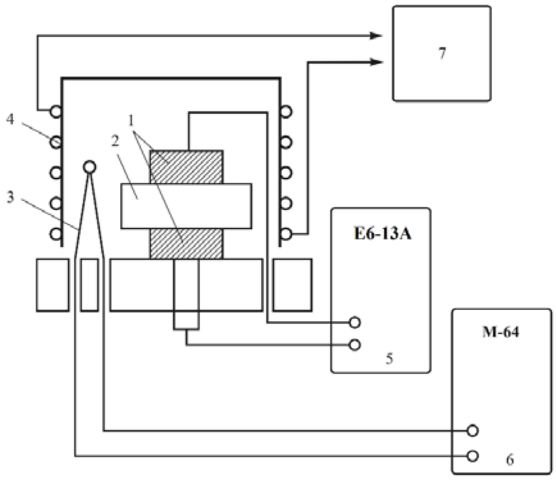

Fig. 1. Block diagram of the device for measuring dielectric permittivity and dielectric losses: 1- the measuring cell, 2 – sample, 3 - thermocouple, 4- heater, 5 - immittance meter, 6- thermometer, 7- automatic three-phase controlling system

Dielectric loss tangent $tg\delta$ is measured directly by the scheme shown on Figure 1. Thus, for each of the selected sample is measured capacitance and the dielectric loss tangent of the angle corresponding to the frequency 1 kHz.

Research of the micro-relief of the surface of composites LDPE + x.vol.% FS were conducted by atomic-force microscope, using specially prepared probes in the form of needle. The working part of the probe has a size of about 10 nm. The typical distance between the probe and sample surface in scanning probe microscopes in order of magnitude is of 0.1 - 10 nm. The operation of scanning probe microscopes are different types of probe-surface interaction. The probe at first moves along the straight line, and then in the opposite direction, then passes to the next line. The movement of the probe is carried out using the scanner in small increments under the influence of the saw-tooth voltage generated by digital-to-analog converters. Registration of the information on the surface topography is made, as a rule, on a direct passage to the following two conditions: the probe during scanning touched all points of the surface, and at every moment the probe touched the surface only on one point [10].

Experimental results and discussion

Results of the study of the surface for LDPE + x.vol.% FS composites are shown in Fig. 2-4. Composites with fillers x = 1; 5; 7; 10; 15; 20; 30; 50 were investigated. Figures 2-4 show the results of the study of the composites in 2D and 3D modes, and histograms for bio-composites respectively. The results obtained show that LDPE + 5.vol.% FS and LDPE + 7.vol.% FS bio-composites have a well-formed surface (Fig. 2-3 a, b). The results of the study of the surface for LDPE + x.vol.$Bi_{0.5}Sb_{1.5}Te_3$ composites are shown in Fig. 5-7. Composites with fillers x = 3; 5; 7; 10; 15; 20 were studied. Figures 5-7 shows the results of the study of composites in 2D and 3D modes and histograms for composites respectively. The results obtained show that the LDPE + 5.vol.% FS and LDPE + 7.vol.% FS composites have a well-formed surface (Fig. 2-3 a, b).

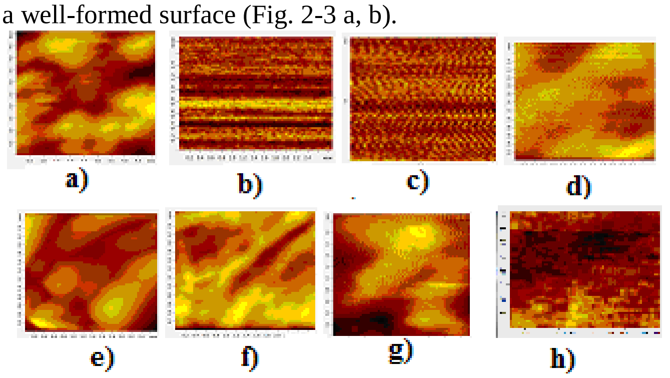

Fig. 2. Longitudinal section of the AFM images in 2D scale. Surfaces of LDPE + x.vol.% FS composites, where a - x = 1; b) - x = 5; c) - x = 7; d) - x = 10; e) - x = 15; f) - x = 20; g) - x = 30; h) - x = 50.

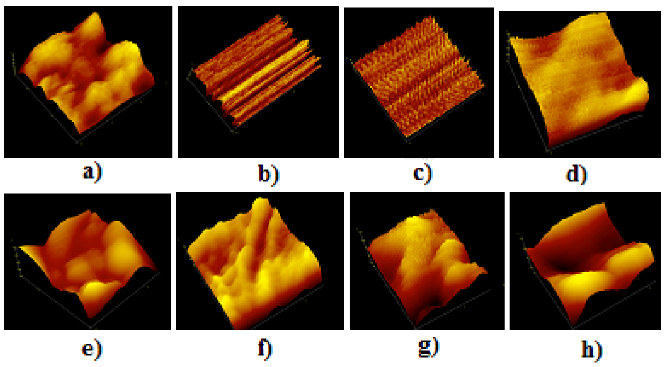

Fig. 3. Fragments of AFM images of surfaces in 3D scale for LDPE + x.vol.% FS composite surface, where a) - x = 1; b) - x = 5; c) - x = 7; d) -x = 10; e) - x = 15; f) - x = 20; g) - x = 30; h) - x = 50.

The research results of study of the dielectric permittivity for LDPE + x.vol.% FS bio-composites are shown in Figure 8, a. Researches were carried out for the composites with fillers 5, 7, 10 and 15 vol.% FS.

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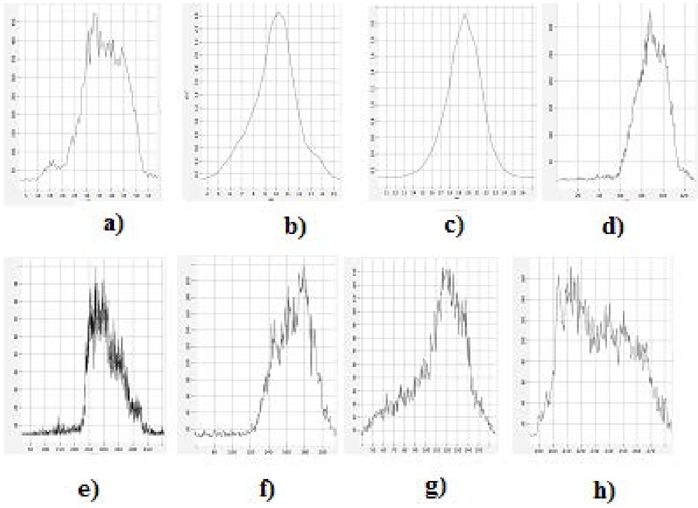

Fig. 4. The histograms for LDPE + x.vol.% FS composites where a) - x = 1; b) - x = 5; c) - x = 7; d) -x = 10; e) - x = 15; f) - x = 20; g) - x = 30; h) - x = 50.

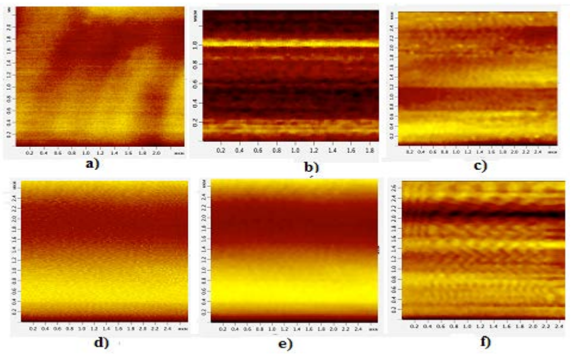

Fig. 5. AFM images of surface in 2D scale for LDPE + x.vol.%$Bi_{0.5}Sb_{1.5}Te_3$ composites, where: a) - x = 3; b) - x = 5; c)-x=7; d)-x=10; e)-x=15; f) - x = 20.

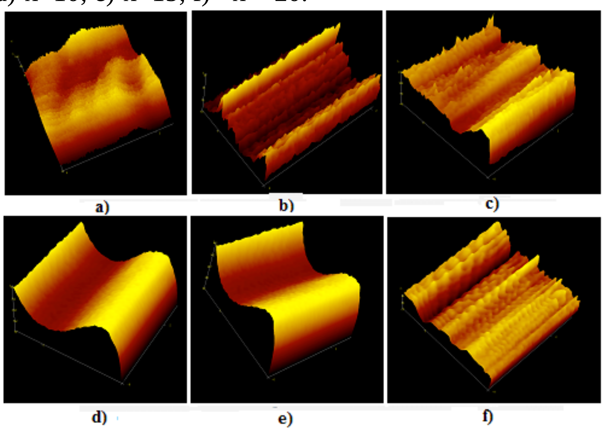

Fig. 6. Fragments of AFM images of surfaces in 3D scale for LDPE + x.vol.% $Bi_{0.5}Sb_{1.5}Te_3$, where a) - x = 3; b)- x = 5; c)- x = 7; d) - x = 10; e) - x = 15; f) - x = 20.

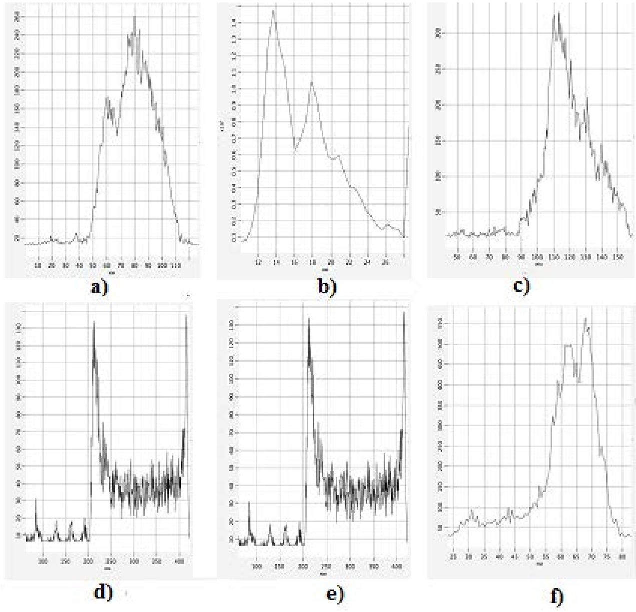

Fig. 7. The histograms for LDPE + x.vol.% $Bi_{0.5}Sb_{1.5}Te_3$ composites, where a) - x = 3; b)- x = 5; c)- x = 7; d)- x = 10; e)- x = 15; f)- x = 20.

The figure shows that in the frequency range 0.5 ÷ 200 kHz typical for all investigated composites dielectric permittivity is constant and in the range of 200 ÷ 1000 kHz increases from 28.37 to 31.69; from 27.72 to 30.45; from 26.44 to 29.72 and from 24.97 to 28.3 for composites with fillers 5, 7, 10 and 15 vol.% FS respectively. In addition, with increasing volume fraction of biological origin filler, the dielectric permittivity is reduced over the entire frequency range.

Figure 8,b is the frequency dependence of the dielectric loss for bio-composites. As follows from the figure, the behavior of the dielectric losses - $tg\delta$ (ν) for the studied composites are identical. In the frequency range of 0.5 ÷ 1 kHz, the dielectric loss ($tg\delta$) greatly increased, and further in the frequency range 1-200 kHz decreases, and finally in the range of 200-1000 kHz increases.

In these composites increasing volumetric filler content leads to an increase in the scale particles in the total thickness of the sample. Closed each other clusters on the sample thickness can be considered as a resistance connected between the electrodes. Since scales have high conductivity compared with LDPE [11], we can assume that the resistance of the composite will be mainly is determined by the contact between the particles and scales. At the boundaries of clusters in an alternating electric field an accumulation and redistribution of free electrical charges is occurred (Maxwell-Wagner volume polarization) which distort the original internal electric field. It is known [12] that at low frequencies the internal electrical field is distributed according conductivity and at high frequencies - respectively the permittivity. Therefore, a slight decrease in ε with increasing measurement frequency can be explained by the creation of relatively strong internal field in scale clusters.

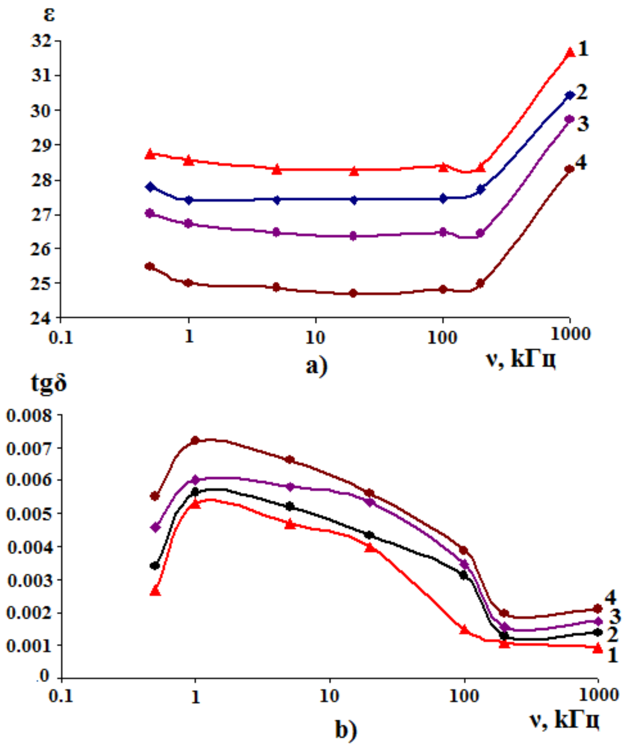

Fig.8. The frequency dependence of dielectric constant (a) and the dielectric loss (b) for LDPE + x.vol.% FS composites, where x = 1 3; 2 = 7; x -3 = 10; 4 x = 15.

The analysis of the dispersion curves (tgδ) shown in Fig. 8.b shows that in studied composites in the measurement range of 0.5 - 1 kHz positive dielectric effect, namely, ascending of tgδ of the samples is observed. At that maximal tgδ for all the investigated composites corresponds to 1 kHz frequency. With increasing frequency, the inertia effect implies in formation of space charge in the composite structure, leading to reduction of the dielectric response. At low frequencies the surface charge has time to follow the field, and the dielectric loss is small. At the high-frequencies polarization have no time to be set for the half-cycle of the field, and dielectric losses are low (Fig. 8b). Observed maximum at a frequency of 1 kHz, is determined. apparently, by relaxation losses, typical for most dielectrics. As relaxation oscillators here may act the structural elements of the composite material with varying degrees of mobility, as well as low molecular weight impurities that appear in the production and processing of the material in result of partial oxidation of polyethylene.

Decreasing of tgδ values with increasing of frequency indicates that at high frequencies 1-200 kHz main type of dielectric losses in these composites are losses in conductivity.

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