

STRUCTURE AND DIELECTRIC PROPERTIES OF NANOCOMPOSITES ON THE BASIS OF HIGH-DENSITY POLYETHYLENE AND LEAD SULFIDE

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Have been studied structures and dielectric properties of nanocomposites on the basis of high-density polyethylene (HDPE) and PbS (HDPE+PbS). By atomic force microscopy method was found that PbS nanoparticles strongly change the morphology of polyethylene and as a result occurs the refinement of surface structural elements. The declining of permittivity ϵ and dielectric loss tangent $\text{tg}\delta$ of nanocomposite with frequency rise is explained with decelerating of dipoles and decreasing of particles number, participating in polarization, i.e. with deterioration of polarization process. Has been observed the strongly pronounced PTCR effect for nanocomposites on the basis HDPE+0.005M PbS.

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1. Introduction

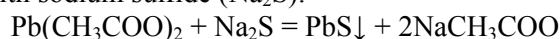
Synthesis, study of structures and properties of polymeric nanocomposites is the priority direction of modern science due to unique properties of nanostructured materials. The complexity of these properties is defined by quantum-size and coulomb effects in nanoparticles and depends on chemical nature, size and shape of particles, distances between them, distribution and ordering. Polymeric nanocomposites attract the attention due to the ability of stabilization of various nanoparticles in polymeric matrix. Applications of polymers with different inductive and semiconductor properties as matrix allow single-minded variation of composite parameters.

Polymeric nanocomposites with semiconductor nanoparticles are able to have unique physical properties, combining the characteristics of semiconductor and polymer films, and the presence of nanoparticles in polymeric matrix bring to principally new effects [1].

The lead sulfide widely applies in infrared optics. At normal conditions the coarse-grained lead sulfide is straight narrowly zoned semiconductor with cubic structure $B1$. At 300K the width of forbidden zone of mono crystalline lead sulfide and semi crystalline coarse-grained films PbS is equal 0.41–0.42 eV [2]. At the last years actively studied the sulfides of lead, cadmium, mercury in nanocrystalline structure. As example was found that at diminishing of size of PbS particles (grains) up to few dozens nanometers the prominent changes of its properties occurs [3,4].

2. Experimental part

The syntheses of nanocomposites on the basis of HDPE and lead sulfide have been carried as follows: for sorption of Pb^{2+} ions the definite quantity of polymeric powder PE was treated by $\text{Pb}(\text{CH}_3\text{COO})_2$ solution in 30 minutes by stirring, then filtered and dried during 24 hours. Then the powder containing Pb^{2+} ions was treated by sodium sulfide solution during 30 minutes, filtered and dried. Then at melting point of HDPE was prepared the film of nanocomposite on the basis of HDPE+PbS. The forming of semiconductor lead sulfide nanoparticles by chemical reaction of lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2$ with sodium sulfide (Na_2S):



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The concentrations of water solution of $\text{Pb}(\text{CH}_3\text{COO})_2$ and (Na_2S) varied in the range 0,0025-0,25M.

The morphology of nanocomposites was studied by AFM method on Integra-Prima (NT-MDT, Zelenograd). For scanning was used special silicon cantilevers, prepared by plasma chemical method of etching, with radius of curvature 20 nm and resonance frequency 1-5 Hz. The scanning area was 1×1 μm . The measurements were carried out at the regime of semicontact microscopy on air, were fixed the changes of oscillation amplitude of needle of cantilever, that defines the topography of surface. The rate of scanning and number of scanned lines on image made correspondingly 1,969 Hz and 256.

The measurements of permittivity and dielectric loss tangent $\text{tg}\delta$ were carried out by using immittance meter MNIPI E7-20. With the use of broadband immittance meter E7-20 was carried out the measurements of frequency dependence of permittivity and dielectric loss tangent $\text{tg}\delta$ at $T=293\text{K}$ in frequency range $f=25-10$ Hz. Temperature dependence of resistivity was measured at voltage 10 V in exposure during 30 min. The temperature changes linearly with 1-3 K/min rate.

3. Results and discussion

It should be noted that polymeric matrix and nanoparticle are able actively interact each other and the degree of its interaction depends on concentration of main phase, nanoparticle size and conditions of nanocomposite preparation. In boundary of phases forms the interphase layer, where the properties are different from the properties of polymeric matrix and nanoparticle [5].

In nanocomposites in such a frontier areas of polymer forms the developed crystalline structure, where appears the structuring activity of nanoparticles, probably due to improvement of thermodynamical conditions of crystallization of molecular chains. The study of structure and dielectric properties of polymeric nanocomposites on the basis HDPE+PbS and ascertainment of correlation of structure and permittivity of nanocomposite is an actual problem.

At picture 1 is given AFM 2D images of surface of HDPE (a) and HDPE +PbS nanocomposite (b) at $1 \times 1 \mu\text{m}$ area.

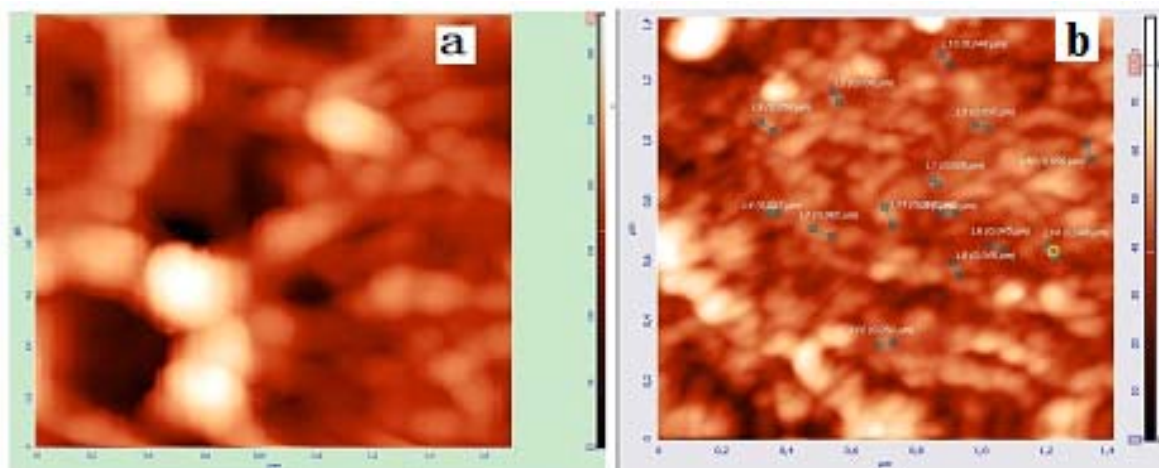


Fig.1 AFM 2D images of surface of HDPE (a) and HDPE +PbS nanocomposite (b)

Was found that PbS nanoparticles strongly changes the morphology of polyethylene, i.e. occurs the refinement of structural elements of surface. Also it is shown that the sizes of PbS nanoparticles is varied 20-50 nm. From picture it is evident that PbS nanoparticles in polymer are homogeneously distributed.

On picture 2 is given the phase contrast of surface of HDPE and nanocomposite HDPE+PbS. On picture 2 (a) it is seen that the surface of polyethylene consists of local ordered structures with definite boundary. The size of these structures make 150-300 nm. On picture 2 (b) it is seen that the surface of nanocomposite consists of ordered structures of polymer 150-300nm and

nanoparticles with definite bounder. On picture 3 is given the 3D image of surface of HDPE and nanocomposite HDPE+PbS. It is shown that PbS nanoparticles strongly changes the morphology of polyethylene, i.e. occurs the refinement of structural elements of surface.

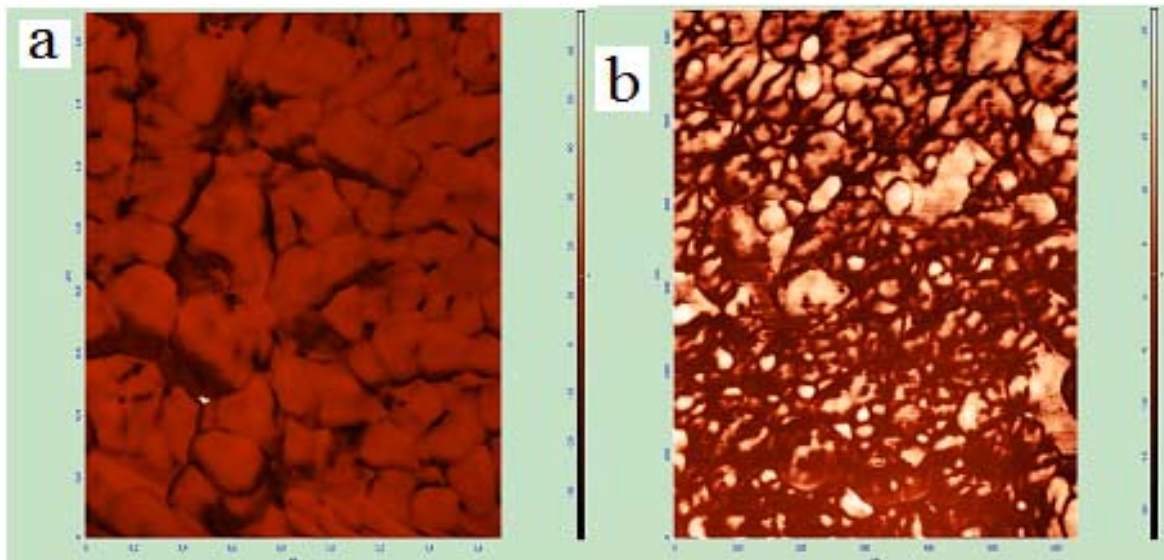


Fig.2 Phase contrast of surface of HDPE (a) and nanocomposite HDPE+PbS (b).

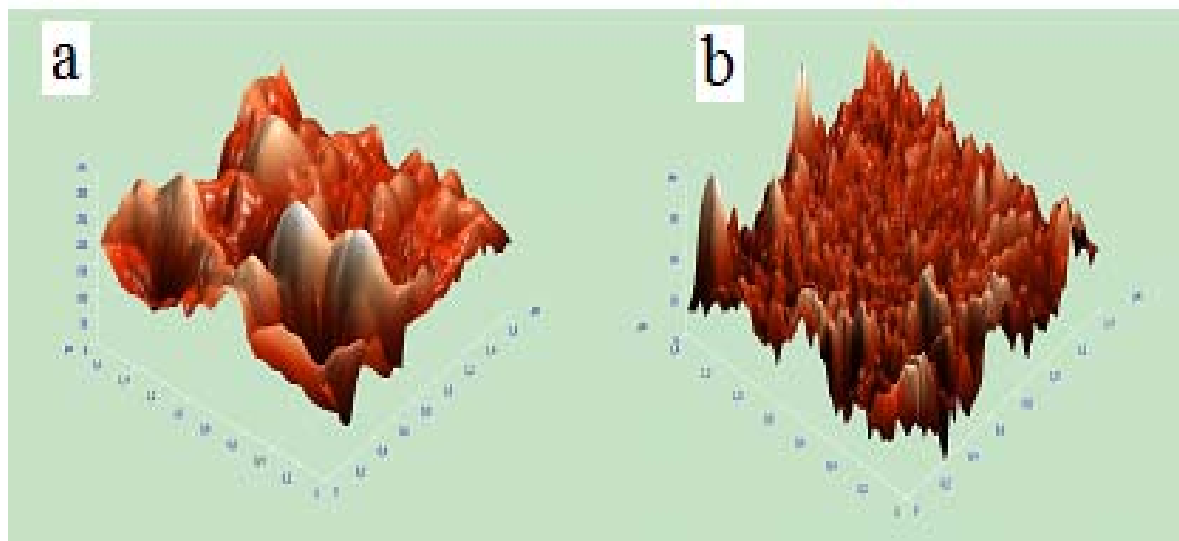
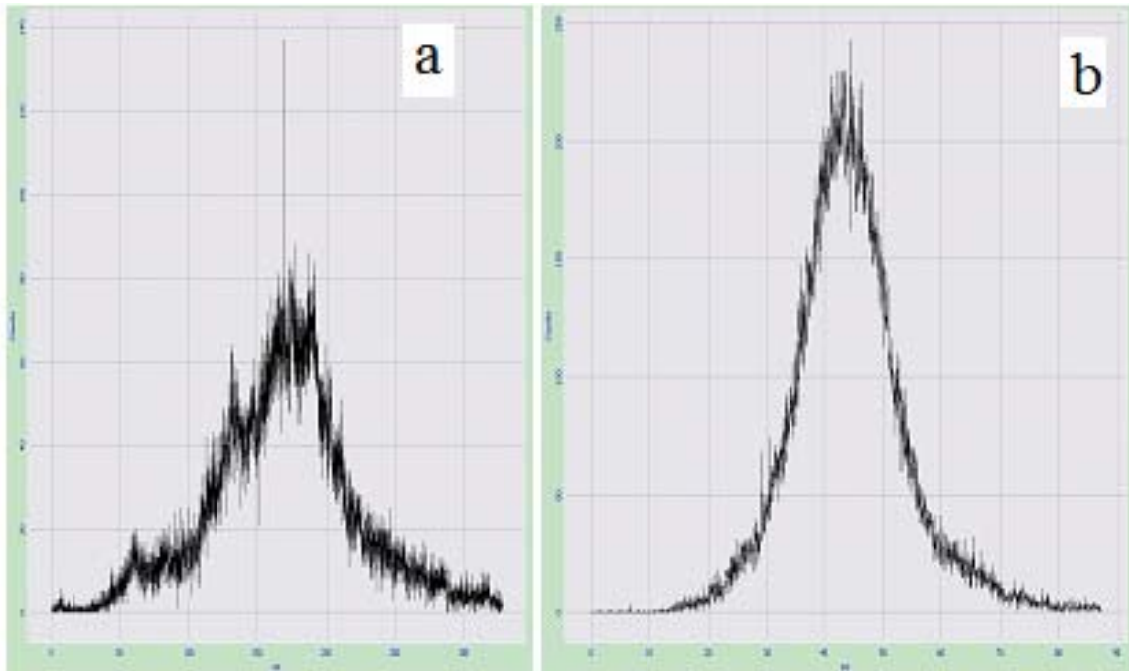


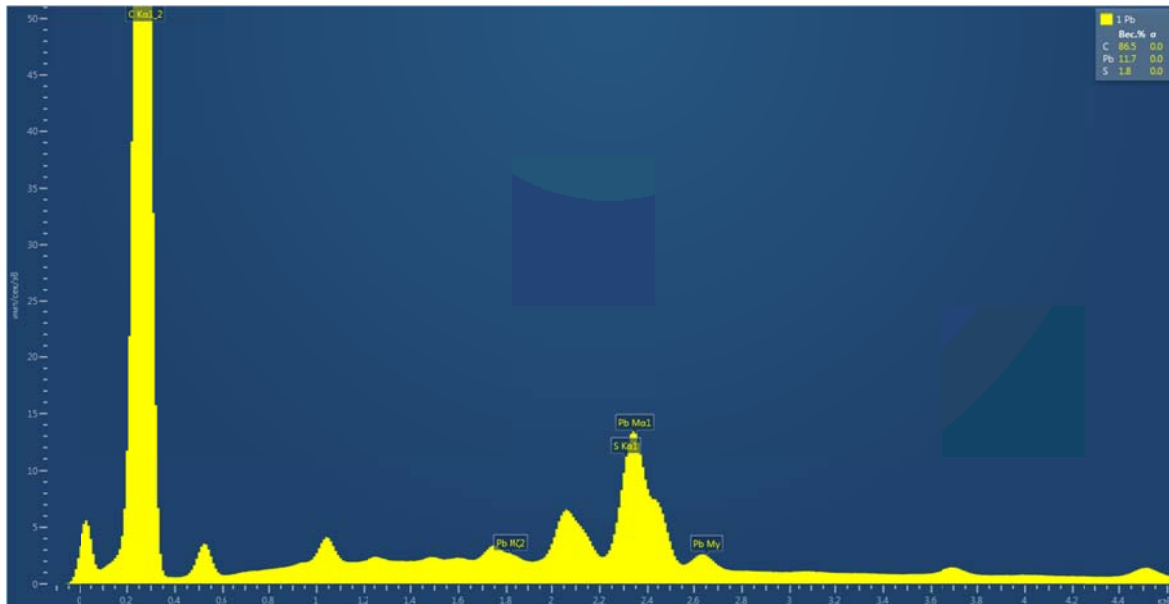
Fig.3 AFM 3D images of surface of HDPE (a) and HDPE+PbS nanocomposite (b)

On Fig. 4 is given the analysis of surface properties and histogram of images elements values of HDPE and nanocomposite HDPE+PbS.



Pic. 4 Histogramms of average surface roughness og HDPE and HDPE +PbS

It is shown that mean-square roughness of surface for HDPE is 200 nm and for nanocomposite HDPE+ PbS is 35 nm. At picture 5 is given the EDX spectra of HDPE+ PbS. It is shown that nanoparticles formed by a polymeric matrix PbS.



Pic.5 EDX spectra of PbS nanoparticles in polymeric matrix HDPE

Have been studied the dependence of permittivity ϵ , dielectric loss tangent $\text{tg}\delta$ of nanocomposite HDPE+PbS from temperature and frequency and also dependence of resistivity and permittivity from temperature. At picture 6 is given the graph of dependence of permittivity ϵ and dielectric loss tangent $\text{tg}\delta$ of nanocomposite HDPE+PbS from frequency. Was found that increasing of PbS nanoparticles in polymer leads to decreasing of permittivity ϵ and dielectric loss tangent $\text{tg}\delta$ rise. It is explained by decreasing of polarizability with rising of conductivity of

nanocomposite. Decreasing of ε and $\text{tg}\delta$ of nanocomposites with increasing of frequency is explained by delay of dipoles and diminishing of particles number, participating in polarization, i.e. with deterioration of polarizing process [6-8].

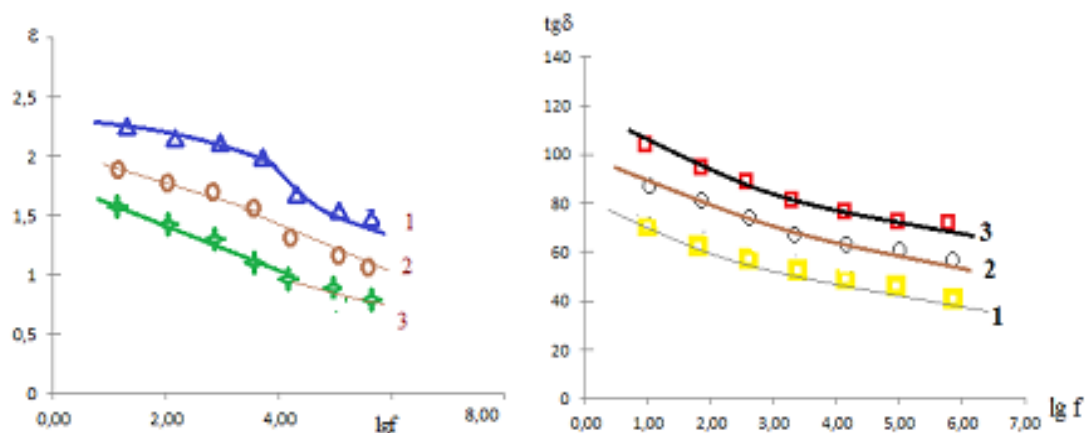


Fig.6 Dependence of permittivity ε and dielectric loss tangent $\text{tg}\delta$ of nanocomposite HDPE+PbS from frequency. 1. HDPE+0,001M PbS, 2. HDPE+0,0025PbS, 3.HDPE+0,005PbS

From experimental data follow the dependence of permittivity from frequency in nanocomposite HDPE+PbS is conditioned by low-frequency polarization. And the monotonous dependence of permittivity from temperature has the relaxation character.

At picture 7 are shown the dependences of permittivity ε and the values of specific resistivity of nanocomposite HDPE+PbS from temperature. Permittivity ε is measured at frequency 1kHz. Experimentally was found that increasing of PbS concentration in polymeric matrix leads to decreasing of permittivity. It is shown that permittivity ε of nanocomposite HDPE+PbS decrease with increasing temperature first slowly, then at 383K comparably faster, and at 398K again slowly.

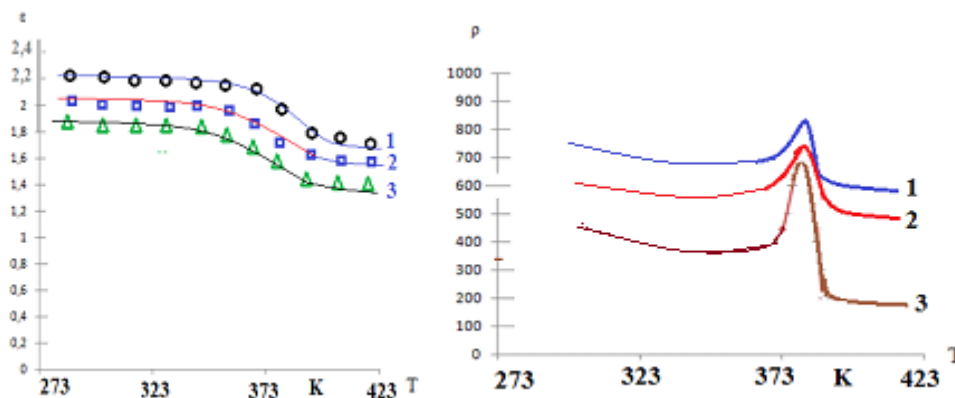


Fig.7 Dependences of permittivity ε and the values of specific resistivity of nanocomposite HDPE+PbS from temperature. 1. HDPE+0,001M PbS, 2. HDPE+0,0025 M PbS, 3.HDPE+0,005 M PbS

On Fig.7 also is given the dependence of ρ from temperature at different concentrations of PbS. In accordance with picture at all concentrations the dependence of ρ first decreases till 373K, and then rapidly raise getting maximum at 383K, and then again decreases. Such rapid increasing of specific resistivity at 383K by our opinion is connected with decomposition of crystalline phase

of polymer. The further increasing of temperature lead to raise of conductivity of polymer, as result the resistance decreases. It is also shown that the value of temperature resistant coefficient (TRC) increases with concentration. For nanocomposite HDPE+0,005 M PbS the strongest pronounced PTCR effect. The studies of dielectric characteristics of composites, obtained at various concentrations of PbS nanoparticles show that properties of composites on the basis polymer-semiconductor depend on specific surface of nanoparticle, chemical activity and properties of frontier interphase layer. The properties of frontier interphase layer depend on electro physical properties of composite components, nanoparticle size, phase interactions of nanocomposites components. So the temperature dependence $\lg\rho=f(T)$ and $\varepsilon=f(T)$ reveal the interaction between degree of permittivity values and volume resistivity of composite.

4. Conclusion

Have been studied structures and dielectric properties of nanocomposites on the basis of high-density polyethylene (HDPE) and PbS (HDPE+PbS). By atomic force microscopy method was found that PbS nanoparticles strongly change the morphology of polyethylene and as a result occurs the refinement of surface structural elements. The declining of permittivity ε and dielectric loss tangent $\operatorname{tg}\delta$ of nanocomposite with frequency rise is explained with decelerating of dipoles and decreasing of particles number, participating in polarization, i.e. with deterioration of polarization process. Has been observed the strongly pronounced PTCR effect for nanocomposites on the basis HDPE+0.005MPbS.

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