

INVESTIGATION THE STRUCTURE AND DIELECTRIC PROPERTIES OF PP+PbS NANOCOMPOSITES SYNTHESIZED ON THE BASIS OF POLYPROPYLENE POLYMER IRRADIATED BY ACCELERATED HEAVY IONS

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Dielectric properties of PP+PbS nanocomposites synthesized on the basis of both pure and irradiated by accelerated heavy ions polypropylene films have been investigated. Experimentally has been found that there is an extreme in the dependence of dielectric permittivity versus irradiation time. Optimum conditions are created for formation of nanoparticles in the matrix and the Pbs nanoparticles are appeared in tracks up to definite value of irradiation time. Increase in irradiation time causes growth of destructive processes and it leads to collapse of a polymeric structure. In turn it yields sharply increase in electrical conductivity and as a result the dielectric permittivity decreases rapidly.

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1. Introduction

Obtaining of regular polymeric nanostructures by ionizing effects (γ -rays, high energy electrons, high speed heavy ions, UV-radiation, electric gas discharge etc.) is widely spreaded technique in comparison with other methods for obtaining the nanostructures with different morphology and properties on the basis of polymeric membranes. Recently various studies reported about sharply variation in both physical and chemical structures of polymeric materials when they were irradiated by the γ -rays, high energy electrons, high speed heavy ions, UV-radiation, electric gas discharge and other types of ionizing radiation.

The constructive, destructive, oxidative processes as well as variation of charge states of polymeric matrices, formation of free radicals, positive ions, hydroxyl, carboxyl and other functional groups can be attributed to variations in chemical structure.

Formation of bonds between molecules (construction), breaking the bonds in main and side chains (destruction), change in unsaturation- appearance and disappearance of double bonds of different nature, formation of internal molecular bonds and processes of radiative oxidation are attributed to the chemical variation of polymer upon its interaction with radiation. Physical variations mainly are the changes in crystallization rate, in a supermolecular structure and physico-mechanical properties of polymer as well as change in the charge state, formation of defects, pores and tracks in a structure of polymeric materials. It should be noted that the rate of change of any property of a polymer is determined by its type and state before irradiation, type and dose of radiation as well as radiation conditions [1].

The radicals and oxidation centers created in polymeric matrix by means of various external radiation sources can play the role of preliminary cells for formation of nanostructures. In these cells the atoms, sulphide and oxide compounds of different metals combine through sorption and form the nanosize clusters.. By variation the sizes of those radicals, oxidation centers and their pores in polymeric matrix one can obtain nanocomposite structures with stabilized physico-

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chemical properties. Hence it is possible to obtain polymeric nanocomposite structures by inserting the metal, metal oxide, and metal sulphide into free radicals and different functional groups. Such a technology leads to formation of regular nanostructures in the volume of polymeric matrix and this plays a great role in the development of sensors, screens and transducers by using these materials. Thus the problem of obtaining of different nanostructures in the composition of polymeric matrix by means of various ionizing effects is becoming more significant [2].

In this paper the PP+PbS nanocomposites were obtained on the basis of isotactic polypropylene, irradiated by accelerated heavy ions and lead sulphide nanoparticles. The structures and dielectric properties of these nanocomposites have been investigated.

2. Experimental part

Polypropylene (PP) film samples have been prepared by hot thermal pressing method from isotactic polypropylene powder with particles of 0.5-1.0 micron size. The PP film samples were irradiated by Xe ions beam with energy 1.3 MeV at flow from 108 up to 1010 ion/cm² on cyclotron AC-100 in the laboratory of nuclear reaction JINR. The irradiated films were treated by 0.5 M and 1.5 M aqueous solution of KOH at 80°C for one hour [1]. The polymer+PbS nanocomposites were prepared via stirring of a certain amount of the previously irradiated PP film in Pb(AsO)₂ solutions with various concentrations (0,001M; 0,0025M; 0,005M; 0,01M; 0,05M vð 0,25M) for 30 min using a magnetic stirrer; after that, the film washed with water to remove the weakly bound Pb²⁺ ions. Next, this film was treated in Na₂S solutions with various concentrations (0.001M; 0.0025M; 0.005M; 0.01M; 0.05 vð 0.25M) during 30 min. The nanocomposite films were dried for a day [3].

The formation of semiconductor lead sulfide nanoparticles in a polymeric matrix occurs by the chemical reaction between lead acetate Pb(CH₃COO)₂ and sodium sulfide (Na₂S) solutions:



SEM analysis of polymer nanocomposite samples were taken on Scanning Electron Microscope JEOL JSM-7600F at an accelerating voltage of 10 kV, SEI regime.

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 5×5 mcm. 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 were 1,969 Hz and 256 respectively.

The measurements of permittivity and dielectric loss tangent tan δ 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 tgδ at T=293K in frequency range f=25Hz-10 MHz. 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

In the Fig.1 are presented the SEM images of PbS nanowires formatted in polypropylene matrix. Also, it is clearly seen from EDS spectra that the nanowires formed in a polymeric matrix are namely the lead sulfide nanoparticles.

In the polymeric matrix occur tracks as a result of bombing of polymeric matrix by heavy ions. The forming tracks have homogeneous structure and this allow obtaining inside of these

tracks the PbS quantum wires, having the uniform diameter. As can be seen from figure the wires are uniformly distributed over the surface. In membranes obtained as a result of bombardment by heavy ions the PbS quantum wires are nano-sized in diameter and micro-sized in length.

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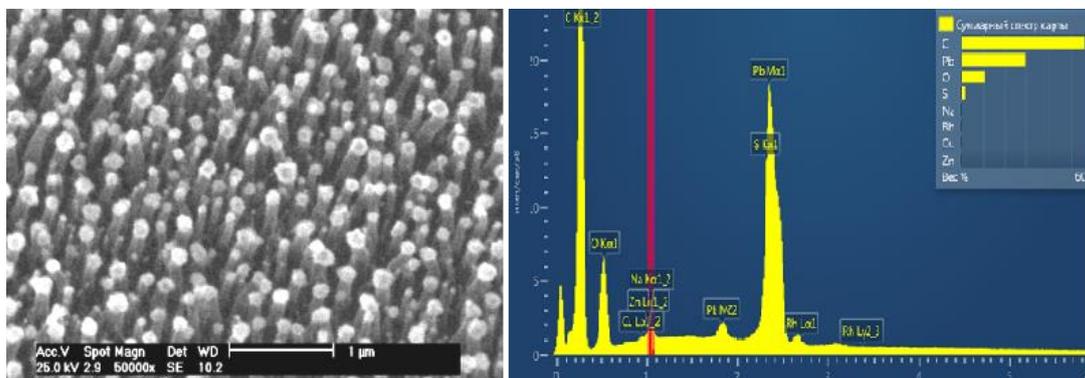


Fig. 1. SEM image and EDS spectrum of PP+PbS nanocomposite

In Fig.2. the AFM images of PP+PbS nanoparticles are demonstrated. It is known that processing of polymer due to its irradiation promotes formation of active centers, radicals, defects and tracks creating optimum conditions for formation of the PbS nanoparticles in the free bulk of polymeric matrix[4-6].

The synthesized PP+PbS nanocomposites have been studied by Atomic Force Microscope. Experimentally has been found that sizes of nanoparticles in polymeric matrix depend on the sizes of free volumes existed in polymeric matrix. It was also found that concentration of nanoparticles increases, but their sizes remain constant as a function of irradiation time. The sizes of PbS nanoparticles are found to be about 15-20 nm.

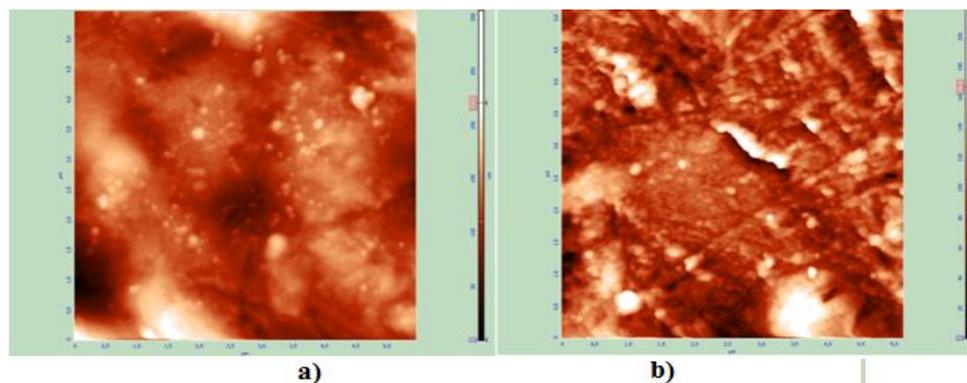


Fig.2. AFM images of PP based PP+PbS nanocomposites obtained from PP, irradiated by Xe heavy ions for one and three hours respectively

Dielectric properties of PP+PbS nanocomposites synthesized on the basis of polypropylene, which irradiated by Xe heavy ions have been studied as a function of frequency and temperature.

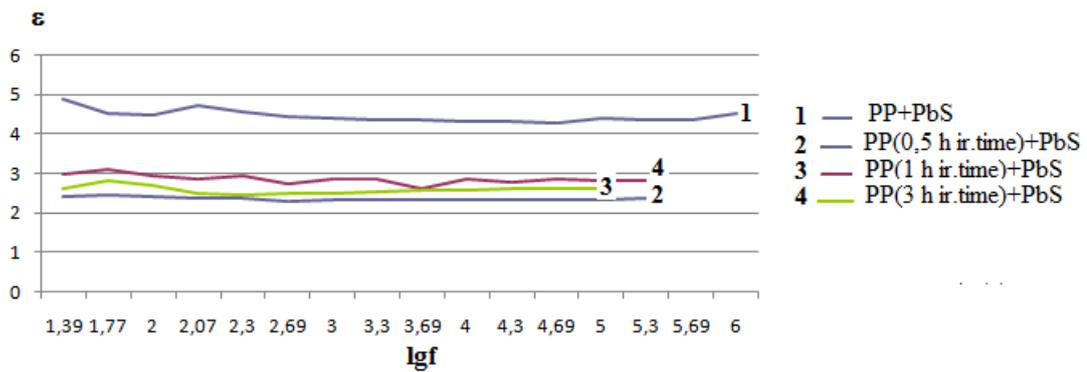


Fig. 3. Frequency dependence of dielectric permittivity for PP based PP+0,005M PbS nanocomposites irradiated by Xe heavy ions at different time intervals

In Fig.3.and Fig.4 are presented frequency dependences for dielectric permittivity and dielectric losses of PP+PbS nanocomposites obtained in polymeric matrix irradiated during different time intervals. As can be seen from Fig.3 variation in magnitude of dielectric permittivity with frequency is negligible, however dielectric permittivity of PP+PbS nanocomposites affected by heavy ions during various time intervals reduces depending on the irradiation tie.

Variation of dielectric losses versus frequency sharply depends on the irradiation time of polymer powder by heavy ions. Values of dielectric losses are near to each other at higher frequencies.

At different frequencies variation of dielectric permittivity versus irradiation time of polymeric matrix is explained by its increase due to formation of quazistable and stable radicals as well as growth of defects and tracks in a polymeric matrix.

Electrical conductivity of polymeric matrix increases to a certain value irradiation time and it causes rise in dielectric permittivity. Determination the period of time of rise in polymer's electrical conductance and destruction processes leads to optimization of the obtaining conditions of nanocomposite.

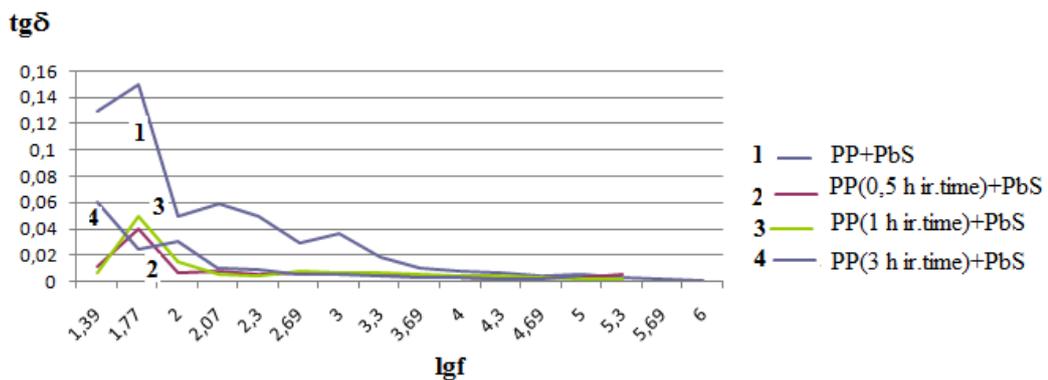


Fig.4. Frequency dependence of tangent of dielectric losses for PP+0,005M PbS nanocomposites on the basis of PP irradiated by Xe heavy ions at different time intervals

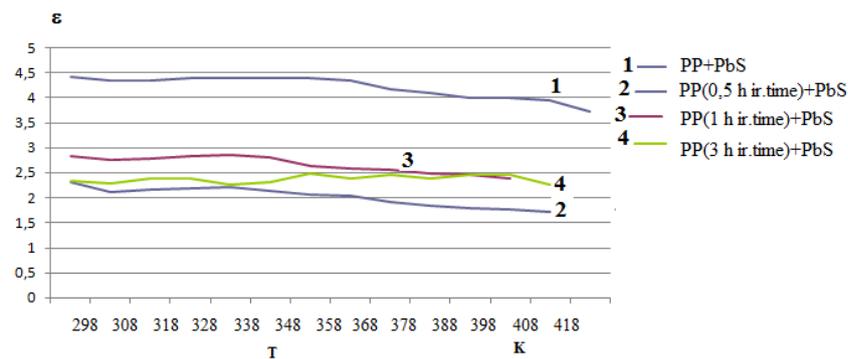


Fig.5. Temperature dependence of dielectric permittivity for $PP+0,005M$ PbS nanocomposites on the basis of PP irradiated by Xe heavy ions at different time intervals

At the same time depending on the irradiation time an increase in concentration of charge carriers in the volume of polymeric matrix causes rise in concentration of PbS nanoparticles in oxidation centers. Existence of extremum in the dependence of dielectric permittivity of PbS nanocomposites versus irradiation time was observed. Such a behaviour in the variation of dielectric permittivity of nanocomposites obtained on the basis of irradiated polymeric films is explained by the change in electric conductivity.

It was experimentally found that there is extremum in the dependence of dielectric permittivity on the irradiation time. Optimum condition for formation of nanoparticles in matrix is created up to definite value of irradiation time, meaning that PbS nanoparticles are formed in quazistable radicals.

Increase in irradiation time causes growth of destructive processes that leads to collapse of polymeric structure. In turn the collapse of polymeric structure leads to sharply increase in electric conductance and hence to rapidly decrease in dielectric permittivity [7].

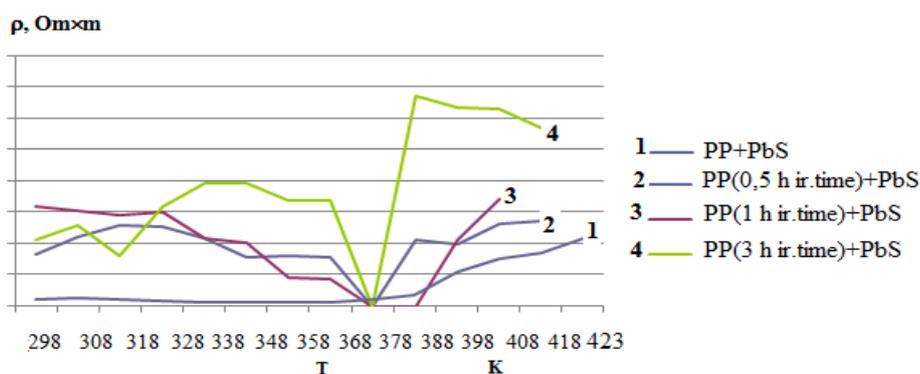


Fig.6. Temperature dependence of resistance of PP based $PP+0,005M$ PbS nanocomposites irradiated by Xe heavy ions at different time intervals

4. Conclusions

Have been studied the structure and electro-physical properties PP+PbS nanocomposites synthesized on the basis of polypropylene films irradiated and non irradiated by accelerated heavy Xe ions. It was found that variation of dielectric permittivity of nanocomposite versus frequency is negligible, however dielectric permittivity of PP+PbS nanocomposites on the basis of PP irradiated by heavy Xe ions at different time intervals reduces as a function of gas discharge duration. At lower values of concentration the PbS nanoparticles play the role of structural formator in a polyeric matrix. As a result the polar groups as well as the stable electrical traps for electric charges are created in the obtained nanocomposites that leads to increase in dielectric

permittivity or improvement the polarizability of these materials. Since nanoparticles behave themselves as individual disperse phase and structural formators upon further increase in concentration their dielectric permittivity becomes larger than that of pure polypropylene. However dielectric permittivity of polymer reduces since its electrical conductivity increases.

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