Chalcogenide Letters Vol. 13, No. 1, January 2016, p. 35 - 40

A STRUCTURE AND DIELECTRIC PROPERTIES OF POLYMER NANOCOMPOSITES ON THE BASE OF ISOTACTIC POLYPROPYLENE AND LEAD SULPHIDE NANOPARTICLES

A.M.MAHARRAMOV, M.A.RAMAZANOV*, F.V.HAJIYEVA
Baku State University, 23 Z.Khalilov str., Baku city, AZ 1148

In the paper reported the ressults of synthesis of polymer nanocomposites on the basis of lead sulphide nanoparticles and isotactic polypropylene. A structure and dielectric properties of synthezied nanocomposites have been investigated. It was determined that at lower concentrations the PbS nanoparticles play the role of structure maker and in prepared nanocomposites formed stable electrical traps for polar groups and electric charges. Formation the stable electric traps for new polar groups and electric charges leads to increase dielectric permitivity and improve polarizability in obtained nanocomposites. A further increase of PbS nanoparticles concentration leads to increasing of conductivity and gradual decreasing of polarizing ability of nanocomposite due to nanoparticles behave as a individual phase.

(Recieved October 12, 2015; Accepted January 15, 2016)

Keywords: Nanocomposites, Polypropylene, Lead sulphide, Nanoparticle, Scanning electron microscope, Supramolecular structure, Dielectric permittivity

1.Introduction

In recent years a synthesis of polymer nanocomposites with unique properties is considered to be an actual problem of material science. In general, unique features of nanoparticles are defined by the quantum-size effects and depend on the chemical nature, size and shape of particles, a distance between them, distribution due to sizes and regularity of their structure. Polymer nanocomposites attract attention in term of the possibility of stabiliziing the different nanoparticles in a polymer matrix. The use of various polymers having both dielectric and semiconductor properties as a matrix allows to purpously change the parameters (properties) of nanocomposite. Development the new methods for synthesis of polymer nanocomposites, investigation their structure and features is of interest from both fundamental and practical points of view. By changing the synthesis conditions and mutual interaction between structure of nanocomposites components and controlling the synthesis process one can obtain the material with desired properties [1].

Lead sulphide is widely used in an infrared technique as well as in micro-and optoelectronics. The electrical properties of the lead sulphide significantly change upon transition from bulk crystalline to nanocrystalline state as in case with other semiconductors. This fact promises new opportunites for the use of its optical features in the visible and infrared regions. As a narrow band semicoinductor the lead sulphide is widely used for the obtaining of temperature sensitive transducers, detectors operationg in the infrared region(850-3100nm) of spectrum, photoresistors and selective sensors. Properties of lead sulphide are significantly change with decrease in nanoparticles' sizes up to nanometer range. Therefore an obtaining of more smaller lead sulphide

* Corresponding author: mamed_r50@mail.ru

nanoparticles and the polymer nanocomposite materials on their basis is of great scientific and practical interest [2,3,4].

In the present paper given the results of synthesis nanocomposite on the basis of izotactic PP+PbS and studied its structure and dielectric properties.

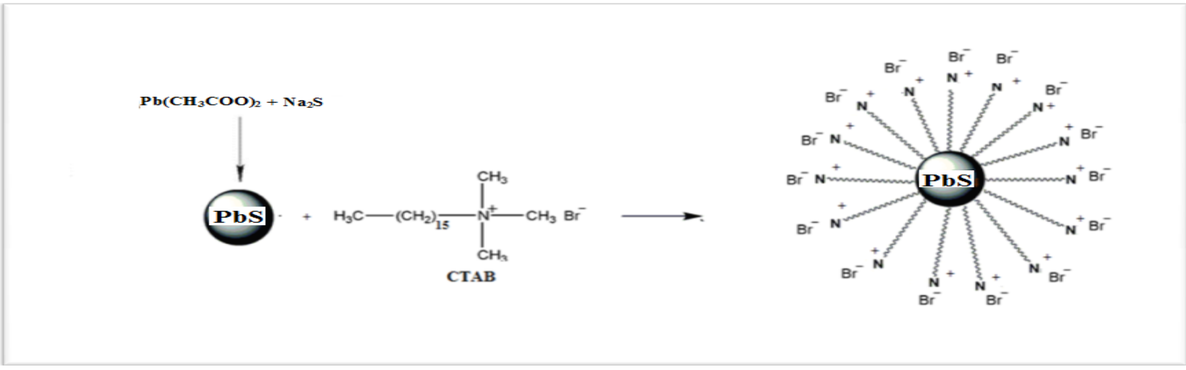
2. Experimental part

In this work the polymer nanocomposites were synthezied in the following manner.

First, were synthesized lead sulfide nanoparticles in the presence of a cationic surface active substance - the cetyltrimethylammonium bromide (CTAB). The PbS nanoparticles were synthezied in presence CTAB as follows: 50 ml 0,25 M lead asetate ($Pb(AcO)_2$) solution was stirred with 30 ml 0,5% CTAB solution in a magnetic mixer during 10 minutes. Further solution of 50 ml 0,25 M sodium sulphide (Na_2S) was added to the primary solution and was intensely stirred at 70-80^{0}C temperature during two hours. The PbS separated from the obtained solution, was washed for several times in the distilled water and dried during one day. The obtained PbS nano-powders were mechanically grinded by crusher in a mortar.

A synthesis process for semiconductor PbS nanoparticles was carried out according the following reaction:

$$Pb(CH_3COO)_2 + Na_2S = PbS\downarrow + 2CH_3COONa$$



Scheme 1. Synthesis of lead sulphide nanoparticles

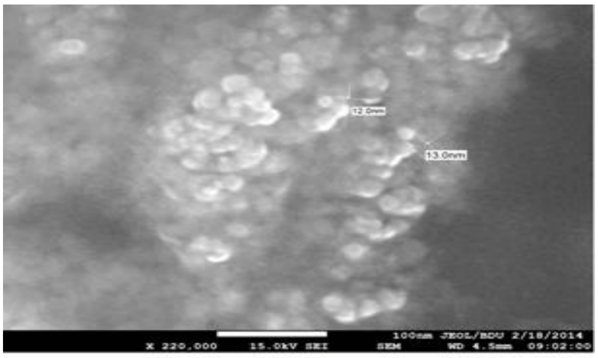
The polymer+PbS nanocomposites were obtained by addition the stabilizied PbS nanopowders to the polypropylene (PP) polymer. First the polypropylene powder of 0,5 g mass has been resolved in 50 ml toluol solvent at 120^0-150^{0}C temperature. Then PbS nanopowders of various amounts were added to the polypropylene (PP) solution and was intensely stirred until the homogeneous compound formation. Samples were transferred to a Petri dish and dried for one day. In order to remove the solvent samples were vacuum dried at a temperature below the melting point of polypropylene. Nanocomposite samples were prepared from these powders by hot pressing at the melting temperature of PP and a pressure of 10 MPa. Analysis of PbS nano-particles has been carried out by scanning electron microscope (Jeol JSM-7600 F) with 15keV energy at operational distance of 4,5mm.

The morphology of nanocomposites has been studied by AFM method on Integra-Prima (NT-MDT, Zelenograd). For scanning was used a special silicon cantilevers, prepared by plasma chemical method of etching, with 20 nm radius of curvature and 1-5 Hz resonance frequency. Sizes of scanning area were 1×1 μm. The measurements have been carried out at the regime of semi-contact microscopy in the air, were fixed the changes in amplitude of oscillation of cantilever's needle, 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 dielectric permittivity and resistivity have been carried out by using the immittance meter MNIPI E7-20. Temperature dependence of resistivity and dielectric permittivity was measured at 10V voltage in exposure during 30 min. The rate of linear variation in temperature was 1-3 K/min.

3. Results and discussion

The sizes of synthezied PbS nanoparticles were studied at scanning electron microscope and it was found that sizes of stabilizied nanoparticles in the presence CTAB is 12-13 nm. (Fig.1)



a)

Fig. 1. The SEM images of CTAB stabilizied PbS nanoparticles.

The element analysis has been carried out for the matter in Fig.2 and it was determined that the compound investigated from this field belongs to the PbS nanoparticles.

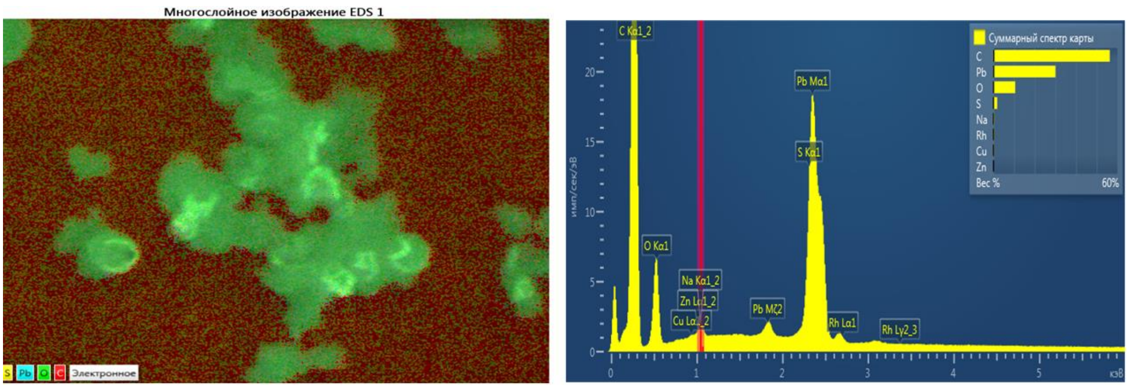


Fig. 2. Mapping images for PbS nanoparticles.

Fig.3 demonstrates the AFM images of pure PP and nanocomposite on the base PP+0,25M PbS and PP+0,5M PbS. As can be seen after the addition of nanosized powders into a polymer matrix occurs a change in the supramolecular structure of polypropylene and refinement of structural elements of surface. The AFM studies show that roughness of surface decreases for 0,25M amount of nanoparticles and its rise is again observed for 0,5M amount PbS (Fig.4).

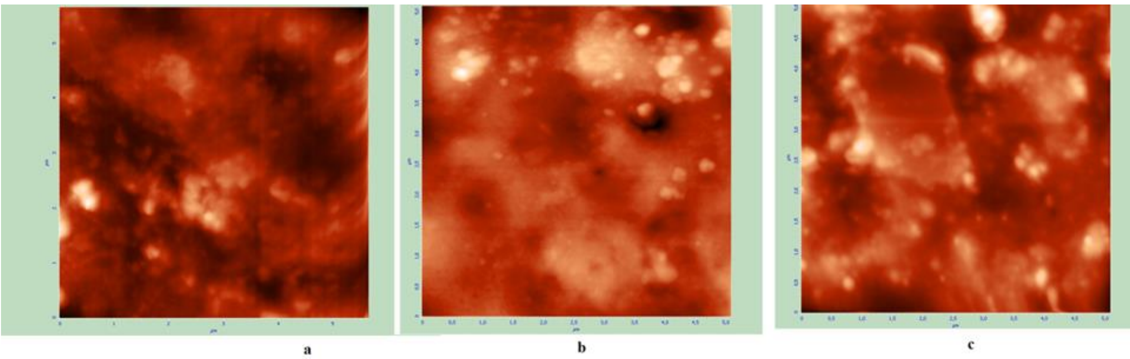


Fig. 3. AFM image of surface polypropylene and PP+PbS nanocomposite
a) PP, b) PP+0,25M PbS; C PP+0,5M PbS

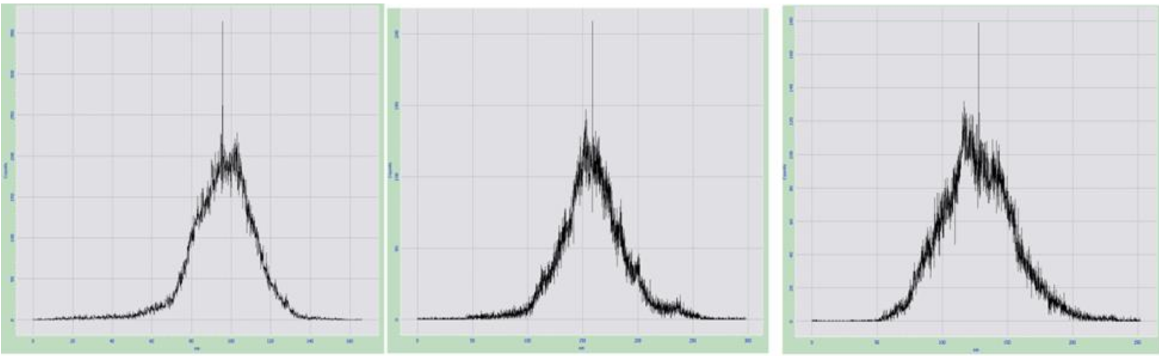


Fig. 4. The surface histograms for PP and PP+PbS nanocomposite.

a) PP, b) PP+0,25M PbS c) PP+0,5M PbS

Dielectric properties of synthezied PP+PbS nanocomposites have been investigated. From the dependence of dielectric permittivity of PP+PbS nanocomposites on the temperature is seen that dielectric permittivity remains practically unchangeable when nanocomposite is heated from room temperature up to 403K and variation in its values is observed above this temperature. Dielectric permittivity of nanocomposition has larger values and its variation for both polypropylene and PP+0,25M PbS is negligible in the all temperature interval (Fig 5.). In Fig.5 an enhancement in dielectric permitivity shows the increase in polarizability of nanocomposites.

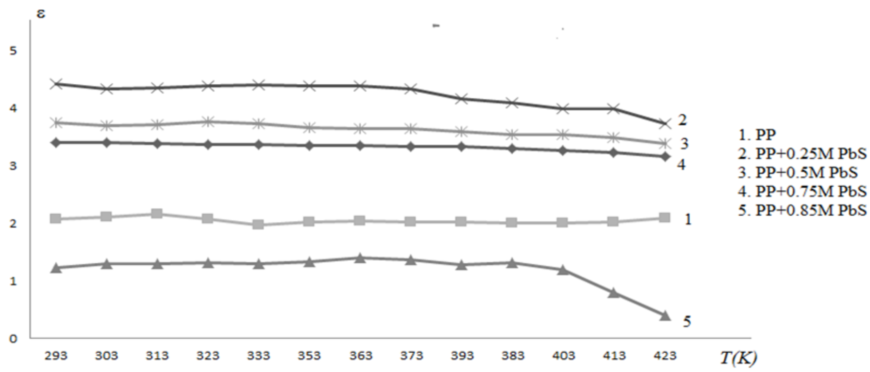


Fig. 5. Temperature dependence of dielectric permitivity for PP+PbS nanocomposites

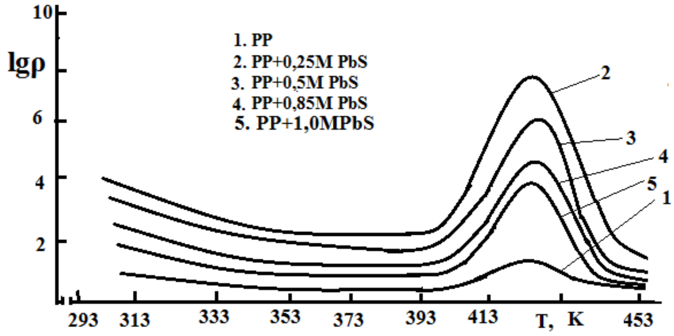


Fig. 6. Temperature dependence of resistivity for PP+PbS nanocomposites

In Fig.6 are presented the resistivity-temperature dependences for PP+PbS nanocomposites. It is seen that there is no significant variation in resistivity versus temperature of polypropylene. However resistivity of PP+PbS nanocomposites varies sharply in a definite temperature interval that indicates observation of the posistor effect in nanocomposites. Rise in temperature leads to increasing a distance between particles due to destroy the crystalline structure in polymer phase and it causes sharply increase in resistance.

From above mentioned one can conclude that the PbS nanoparticles of 0,25M amount play the role of structure formator and nanoparticles behave as the second phase upon further increase of concentration. It should be noted that the polymer matrix and nanoparticles may be in an active mutual interaction depending on the concentration of main phase, sizes of nanoparticles and conditions of its synthesis. In nanocomposites a crystalline structure is formed in the transition region of polymer's boundary layer, it leads to increasing of constructive activity of nanoparticles and improoving of thermodynamic conditions for crystallization of molecular chains of boundary layer.

4. Conclusions

In this paper reported the synthesis of nanocomposites based on isotactic polypropylene and lead sulfide nanoparticles The AFM studies of nanocomposites show that after the addition of nanosized powders PbS into a polymer matrix occurs a change in the supramolecular structure of polypropylene and refinement of structural elements of surface. The dielectric permittivity after addition of the nanoparticles PbS in the polypropylene varies with the extremum and 0,25 M PbS concentration takes its maximum value. The maximum value of dielectric permittivity at a concentration of 0.25 M PbS is explained by the fact that lead sulphide nanoparticles play the role of crystallization centers. A sharply change of resistance of nanocomposites in dependance of temperature is explained by the increasing of distance between particles due to destroy of crystalline structure in polymer phase at 413-423 K temperature interval.

References

[1] A.D.Pomogaylo, A.S.Rozenberg, I.E.Uflyand. Metal nanoparticles in polymers. Publ: Chemistry, 2000, p.671

[2] S.I.Sadovnikov, N.S.Kozhevnikova, Solid State Physics, **54**, 1459 (2012).

[3] S.I.Sadovnikov // Nanocrystalline lead sulphide: Synthesis, structure and properties. Autoabstract 2011,p.3-10

[4] Jayesh D. Patel, Frej Mighri, Abdellah Ajji, Said Elkoun//Room Temperature Synthesis of Aminocaproic Acid-Capped Lead Sulphide Nanoparticles.*Materials Sciences and Applications*, 2012, p.125.

[5] A.M.Magerramov, M.A.Ramazanov, F.V.Gadjiyeva The Journal of American Science, **5**(6), 95 (2009) ISSN: 1545-1003
[6] A.M.Magerramov, M.A.Ramazanov, F.V.Hajiyeva J. Optoelectron. Adv. Mater. Rapid Comm. **2**(11), 743 (2008).
[7] B.I.Sazhin // Electrical properties of polymers, PR L., Chemistry, 1986, p. 224