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STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF POLYMER NANOCOMPOSITES ON THE BASIS OF POLYPROPYLENE PP + Ag_2S

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In this paper, presented the results of developing of new nanocomposite structures based on isotactic polypropylene and silver sulphide and studied the distribution of nanoparticles Ag_2S by atomic force (INTEGRA PRIMA) and scanning electron microscopy (SEM, JEOL JSM-7600). Atomic force and electron microscopic study of samples of nanocomposites shows that the developed technology for producing nanocomposites allows obtaining a homogeneous and uniform distribution of silver sulphide nanoparticles in a matrix of polypropylene. It is shown that with increasing concentrations of the starting solutions of reacting salts the Ag_2S nanoparticle size increase in polypropylene matrix, i.e. in the formation of clusters Ag_2S nanoparticles merge as a center of crystallization. Found that with increasing concentration of silver sulphide in the matrix decreases the intensity of the photoluminescence spectra as compared with the spectra of the nanocomposite films with a low concentration of nanoparticles. It is assumed that a significant decrease in the intensity of the luminescence at high concentrations may be due to the phenomenon of concentration quenching and decrease of the specific surface of the nanoparticles in a polymer matrix.

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1. Introduction

Preparation of polymer composites containing nano-sized particles of silver sulphide is a matter of great scientific and practical interest. It is known that zinc and cadmium sulphides exhibit fluorescent properties of [1,2]. Typically, the various organic compounds – dyes are used as luminophores, but in recent years, carried out intensive research for obtaining new nanostructured materials exhibiting fluorescence properties on the basis of nanoparticles of inorganic compounds such as transition metal chalcogenides [3-7]. Particularly promising materials in this regard are polymeric materials modified by transition-metal chalcogenides [8,9].

In recent years, increased interest in nano-sized particles of silver sulphide due to their unique electro, photoelectric and photoluminescence properties [10-15]. Thanks to these properties nanocomposites containing nanoparticles of silver sulphide can be widely used in various devices such as solar cells, as photodetectors, sensors [16-18]. It should be noted that, despite the great potential application of polymer nanocomposites containing nanoparticles of silver sulphide fluorescent properties of these composites have not studied enough yet.The use of these materials is due to the properties of nanoscale particles and often directly dependent on the methods of preparation, as even minor fluctuations preparation technology greatly influence the properties of the synthesized samples [19-20].

Further properties Ag_2S/polymer nanocomposite is very sensitive to the synthesis method and the latter is significantly dependent on the polymer structure. Molecules of polymer matrix have structuring and thus stabilizing effect on the size and distribution of silver sulphide

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nanoparticles in the polymer matrix. For example, there is information about how to obtain a uniformly dispersed silver sulphide nanoparticles in the polymer polyvinylpyrrolidone matrix by electro-spin technique [21]. Authors of [22] used the ultrasound method of producing of silver sulphide nanoparticles in the presence of polyvinyl alcohol. It should be noted that the combination of two synthetic methods, namely ultrasound and microemulsion methods has a number of advantages in terms of producing nanocomposites with new desired properties and improve their exploiting characteristics.

This paper presents a combinational method for the synthesis of nanocomposite Ag_2S/ polypropylene, which combines the application of ultrasound and microemulsion methods and investigated its photoluminescence properties.

2. Experiments and methods

The reagents used in the experiment were analytically pure and does not require further purification. In the experiment, was used twice-distilled water. The reaction flask in which the reaction is conducted under the influence of ultrasonic radiation was purged with nitrogen to displace air.

Were prepared aqueous solutions 0.0025 M, 0.005 M, 0.01 M of$AgNO_3$ and Na_2S salts. Polypropylene powder 0.5 g was dissolved in 50 ml of toluene. 1 ml of the appropriate aqueous solution of the salt in the presence of 0.05 g of sodium lauryl sulphate were mixed with 25 ml of toluene/PP. Every single water microemulsion (solution1)/toluene + PP and (solution2)/toluene + PP was sonicated for 20 min (0.6 cm diameter; Ti-tip; 20kHz; 60W/cm^2) at 30^{0}C temperature supported by a cooling bath. Then, a microemulsion containing (solution2)/PP + toluene was slowly added dropwise water microemulsion (solution1)/PP + toluene at 30^{0}C temperature and an ultrasonic treatment for 30 minutes. At the end of reaction the colour of microemulsion turns dark-grey, and it is explained by the formation of silver sulphide nanoparticles. The resulting dispersion containing nanoparticles of silver sulphide and polypropylene subjected to vacuum evaporation of excess solvent and product was poured onto a glass plate to form a polymer film at room temperature.

By hot pressing at a melting temperature of PP and 10 MPa pressure for 5 minutes and powders produced from these samples nanocomposites. Thus were synthesized nanocomposites with filler content Ag_2S - 0.0025 M, 0.005 M, 0.01 M mass.%. The morphology of the nanocomposites, including the distribution of silver sulphide nanoparticles in the depth of the polymer matrix were investigated by scanning electron (JEOL JSM - 7600F) and atomic force microscopy (AFM INTEGRA PRIMA), and the fluorescent properties of the nanocomposite were studied on spectrofluorimeter Cary Eclipse.

3. Results and discussion

High physical and chemical characteristics of polypropylene, provides a double benefit: first, it increases the shear stress, which lead to the formation of clusters of silver sulphide in the supramolecular structure of the polymer; secondly, the highly viscous nature of polymer structure with a low molecular mobility prevents re-aggregation of silver sulphide nanofillers. Improving the adhesion between the composite components facilitates homogeneous distribution of nanoparticles in the polymer matrix. Electron microscopic examination of samples of nanocomposites shows that the developed technology for producing nanocomposites allows to obtain a homogeneous and uniform distribution of silver sulphide nanoparticles in polypropylene matrix. Samples of the nanocomposites were studied by scanning electron microscopy (SEM, JEOL JSM 7600). Figure 1, 2 and 3 show electron microscopic images based nanocompositesPP +Ag_2S obtained with various contents of silver sulphide nanoparticles.

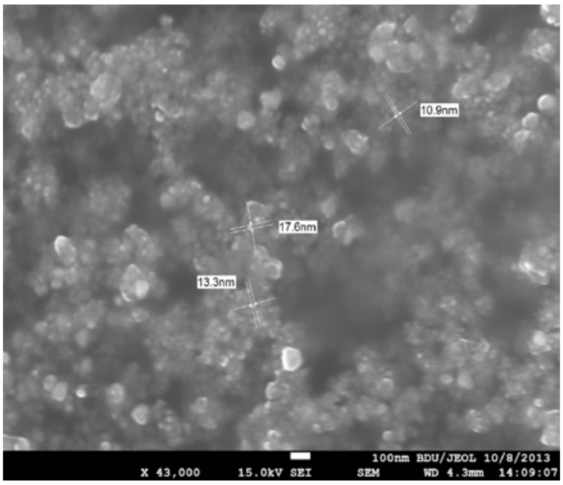

Fig.1. Electron microscope image of nanocomposites PP+Ag_2S at concentration 0.0025M

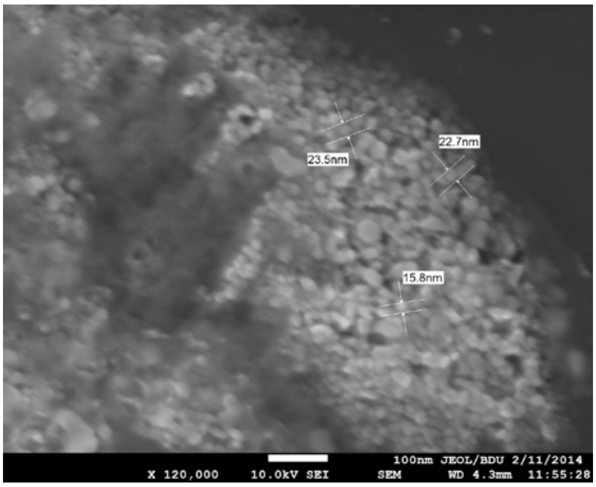

Fig.2. Electron microscope image of nanocomposites PP+Ag_2S at concentration 0.005M

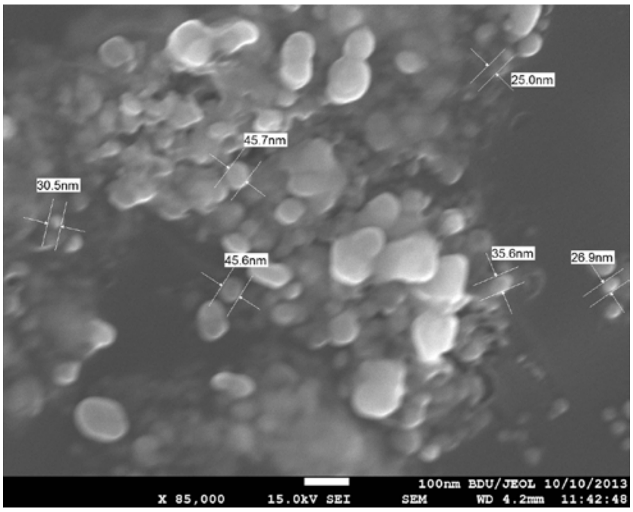

Fig.3. Electron microscope image of nanocomposites based on PP+Ag_2S at concentration 0.01M

From the figures 1, 2, 3 clear that with increasing concentration, the dimensions of silver sulphide Ag_2S nanoparticles increases. Experimental results indicate that with increasing concentrations of the starting salts $AgNO_3$ and Na_2S solutions the size of Ag_2S nanoparticle increase for polypropylene, i.e. in the formation of clusters Ag_2S nanoparticles merge as a centre of crystallization. In our opinion it is due to the fact that increasing concentration of the salts solutions the most of the ions Ag^+ and S^{2-} spent oncoagulation of primary formed Ag_2S nanoparticles but not on the formation of new nuclei. Electron microscopic examination of nanocomposites showed that the distribution of silver sulphide nanoparticles is uniform and homogenous in polypropylene matrix. Experiments show that there is also form silver sulphide nanoparticleswith small sizes in polypropylene matrix at high concentrations of starting salts.

The sample of nanocomposite PP+Ag_2S was analysed and studied the microstructure and elemental composition of the phases. The study of microstructure of the samples is often accompanied micro X-rayanalysis;the characteristic feature of last one is its locality - themaximum excitation region of 1 μkm. This will provide information on the chemical composition of the sample in any selected microscopic site.

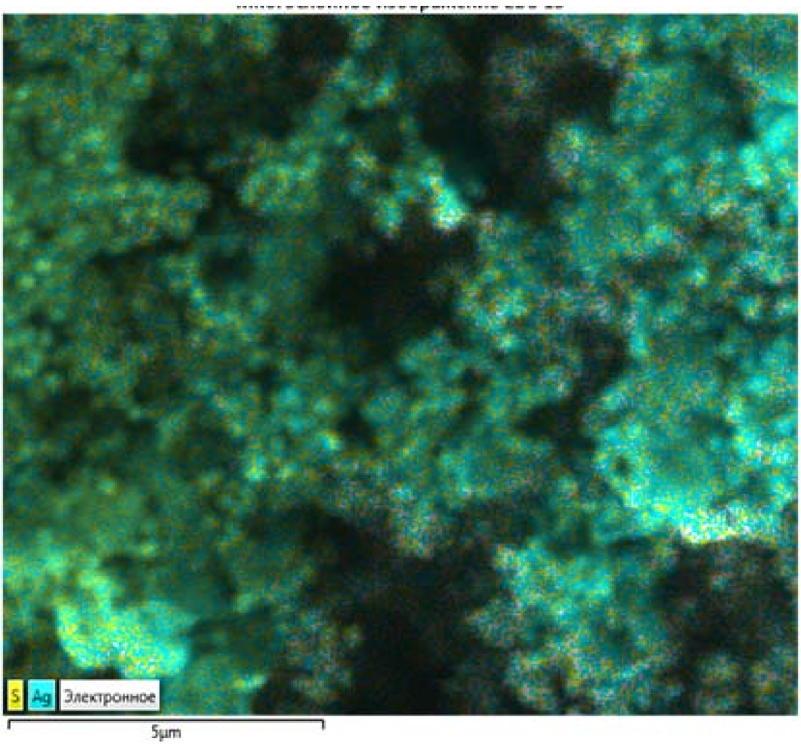

Fig. 4Energydispersivemicro-X-ray analysis of nanocompositePP+Ag_2S

Energydispersive micro-X-ray analysis of nanocomposite PP+$Ag_2S$was performed using energy dispersive spectrometer mode using signals of secondary electrons and backscattering electron. In the case of energy-dispersive spectrometer there is an accumulation of the entire spectrum, so qualitative analysis is automatically performed at any measurement. Energy dispersive spectrometry performs quantitative X-ray microanalysis and spectra obtain predetermined pitch region: point, area, along the line.

Quantitative elemental composition of the six point spectra revealed that the light phase is mainly composed of carbon (67 wt.%), oxygen (18.24 wt%), silver (13.23 wt.%), And the rest - of the other elements. General view of the X-ray spectrum lines, showing the presence of elements in a dark phase is shown in Figure 5.

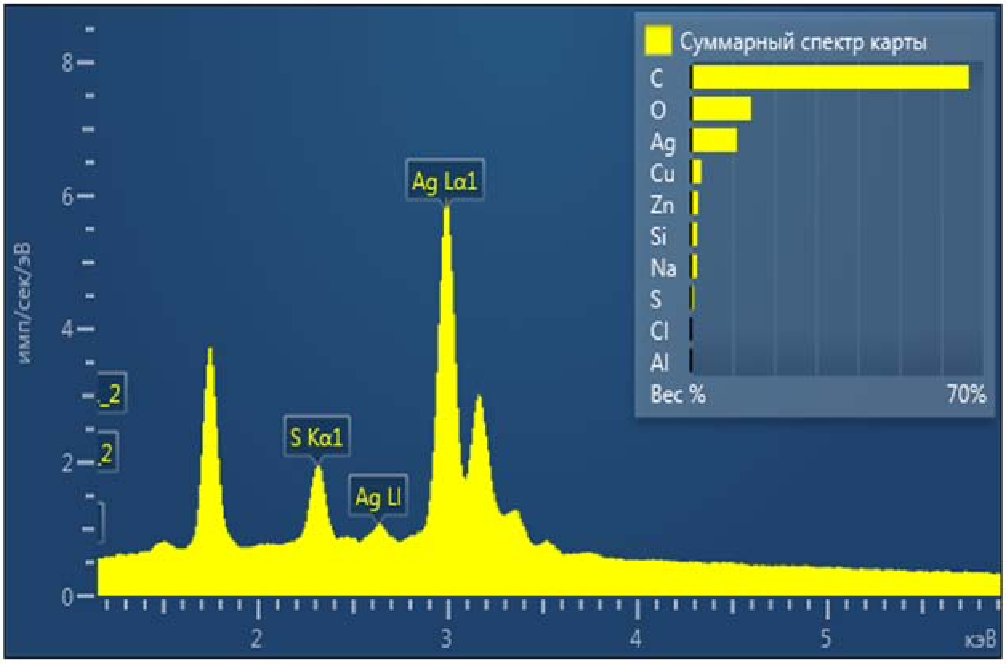

Fig.5 General view of the lines of point X-ray spectrum showing the presence of elements

To confirm the elemental composition of the phase was carried out mapping of the distribution of elements on the surface. (Figure6). If we impose the maps of distribution of the chemical elements (Figure 6) on the microprobe analysis of nanocomposite microstructure (Fig. 4), we find that the light phase consist of three elements C, S, Ag, dark - only from C.

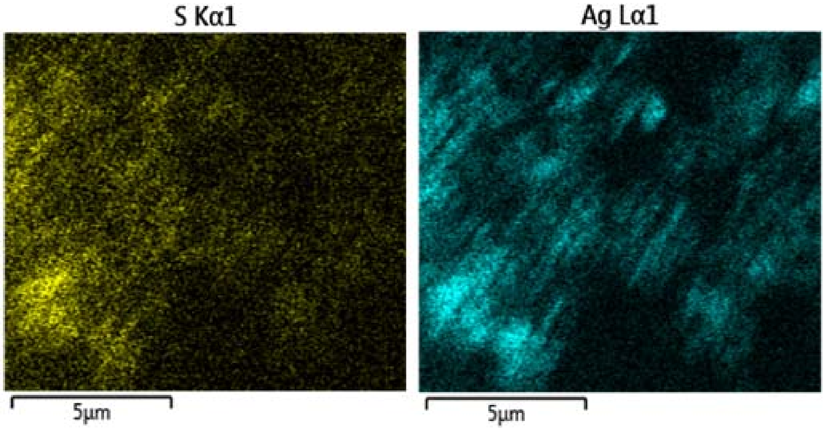

Fig. 6 Mapping of images of nanocomposite sample PP + Ag_2S

The morphology of the nanocomposite PP+Ag_2S and size of distributed Ag_2S nanoparticles wasexamined with a scanning atomic force microscope (AFM) (Figure 7). The figure 7 shows the 2D and 3D images of the nanocomposite. The figure shows that the size of the Ag_2S nanoparticles is approximately 20-60 nm. Atomic force microscopy study also showed that the nanoparticles Ag_2S uniformly distributed in the volume of PP matrix, i.e.in pores of the polymer.

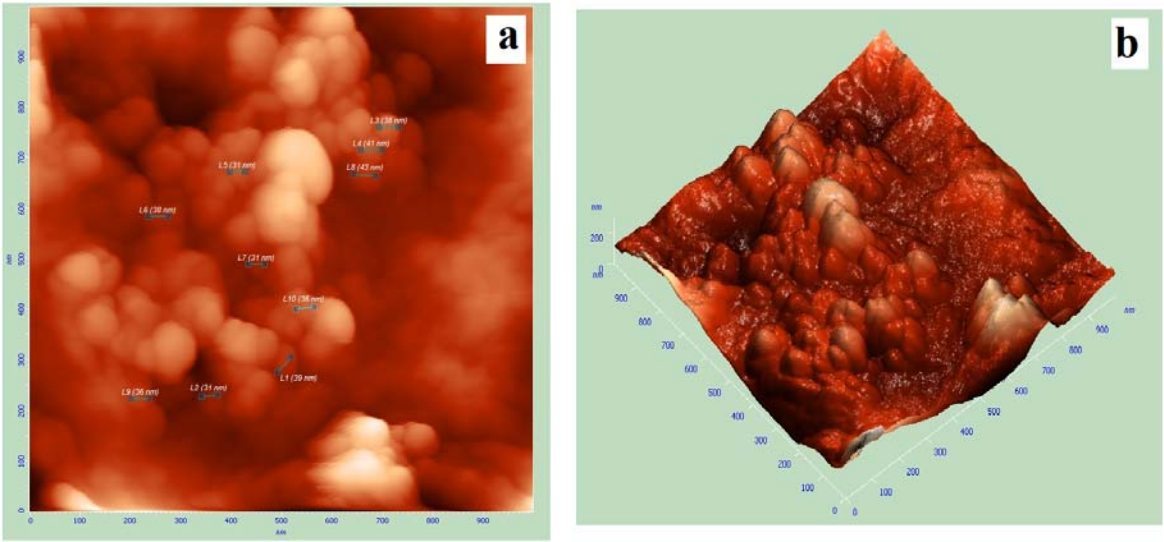

Fig. 7. Nanoparticle size and morphology of the nanocomposite PP+Ag_2S
a) 2D, b) 3D

Photoluminescence spectra were measured in the wavelength range 300-700 nm excited at wavelength 220 nm. Figure 8 shows the luminescence spectra of the nanocomposite PP+Ag_2S.

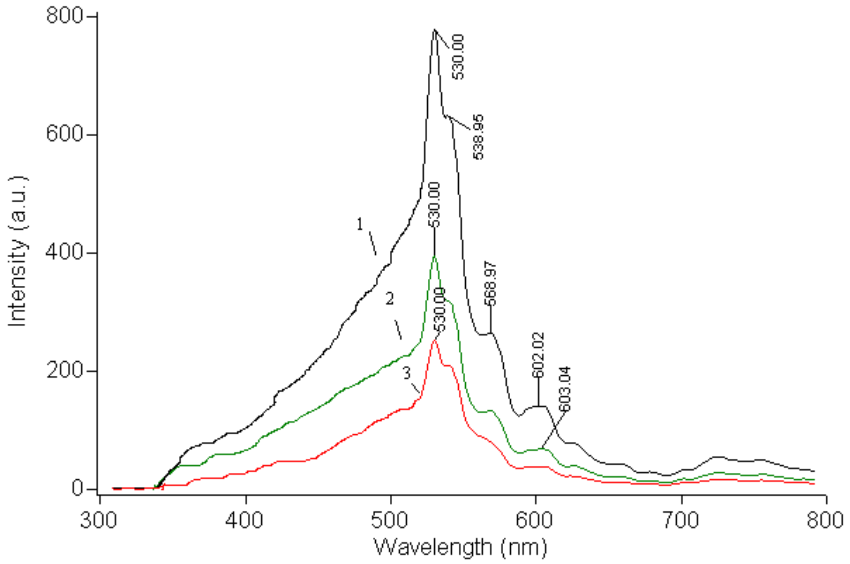

Fig. 8. The PL spectra of the nanocomposite PP+Ag_2S
1. Ag_2S 0.0025M, 2. Ag_2S 0.005M, 3.Ag_2S 0.01M

In steady-state luminescence spectra observed major band with λ_{max}=530нм, λ_{max}=539нм, λ_{max}=568нмиλ_{max} =602нм(Figure 8), which is responsible for the nanoclusters (Ag_2S).It is seen that with increasing concentration of Ag_2S amplitude of the photoluminescence peak at a wavelength decreases. With increasing concentration, i.e. the size of nanoparticles in the matrix also increase and it lead to decreases the intensity of the photoluminescence spectra as compared with the spectra of the films with a small concentration of nanoparticles. A significant decrease in the intensity of the luminescence at high concentrations possibly is due to the phenomenon of concentration quenching and decrease of the specific surface of the nanoparticles in a polymer matrix. It is assumed that the reduction in the intensity of the luminescence at high concentrations can also be interpreted as a result of electron-hole transfer of excitation from one cluster to another (electron remains on a single particle at a time as hole goes on the adjacent particle) due to the electric interaction.

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