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PREPARATION AND STUDY OF NANOCOMPOSITE STRUCTURES BASED ON POLYPROPYLENE AND SILVER SULPHIDE

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In the present paper we used a combination of two synthetic methods for preparation of polypropylene-based nanocomposite and silver sulfide (PP/Ag_2S), by application of ultrasound and microemulsion techniques. The morphology of the nanocomposite and distribution of nanoparticles of silver sulphide in the polymer matrix was studied by atomic force microscopy and scanning electron microscopy. SEM and AFM study of nanocomposite Ag_2S in polypropylene showed that, depending on the dose of γ rays irradiation the concentration of Ag_2S nanoparticles in polypropylene changes. It is found that the size of the nanoparticles at doses of 15 kGy, 30 kGy, 50 kGy is not changed, i.e size of the Ag_2S nanoparticles is 30-40 nm. It is found that with increasing doses of γ radiation polypropylene powders led to decreasing of surface roughness, i.e. occurs the grinding of structural elements of nanocomposite surface. With increasing of γ rays doses increases the proportion of cross-linking that leads to the destruction of the crystalline structure of polypropylene and as a sequence the delaying of the formation of supramolecular structure of polypropylene. Also by IR spectroscopy indicated that γ-ray treatment of polypropylene powders leads to an increase of intensity of oxygenated groups in the structure of polymers, these groups play centre of nucleation to form silver sulfide nanoparticles in polypropylene.

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1. Introduction

The preparation of nanostructured polymeric composite materials based on thermoplastic polymers and semiconductors designed for optoelectronic technology is very important problem. In recent years sharply increased interest to nano-sized particles of silver sulfide stabilized in a polymer matrix [1-2] due to the unique photovoltaic, photoluminescent and electrical properties. It is also known that Ag2S/polymer nanocomposite is very sensitive to the method and condition of the preparation and highly dependent on the polymer structure. Polymer molecules are structuring matrix and thus have a stabilizing effect on the size and distribution of silver sulfide nanoparticles in a polymer matrix. For example, in [3] reported about obtaining of evenly dispersed silver sulfide nanoparticles in the PVP polymer matrix by means of electro-spin technology. The authors of [4] describe of the preparation silver sulfide nanoparticles in the presence of polyvinyl alcohol by using the ultrasound treatment of solution. Synthesis of the nanocomposite based on organic and inorganic compounds allows combining the properties of the individual phases, and significantly improve the characteristics of new materials [5-6]. Using a combination of two synthetic methods, namely ultrasound treatment of the reaction mixture and applying of microemulsion methods has a number of advantages in terms of obtaining new nanocomposites with desired properties and improve their performance.

In this article described the combination of two synthetic methods for preparation of nanocomposite based on polypropylene and silver sulfide (PP/Ag2S) combining the use of

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ultrasound and microemulsion techniques and examined nanocomposite structure depending on γ radiation dose.

2. Methods of Experiment

2.1 Reagents

For research used the powder of isotactic polypropylene powder (M 250000q/mol), silver nitrate ($AgNO_3$), sodium sulfide (Na_2S), toluene ($C_6H_5CH_3$), $C_{12}H_{25}SO_4Na$ - lauryl (dodecyl) sodium sulphate, H_2O - distilled water.

For the obtaining of the nanocomposite PP/Ag2S was used a combination of two synthetic methods – ultrasound and microemulsion techniques. In order to increase activity towards transition metal ions, in particular Ag^+, the polypropylene powder was treated by different doses of γ-rays.

When exposed to γ irradiation in polypropylene form functional oxidative centers. These centers are in turn providing efficient and uniform distribution of metal ions in polymeric matrix: silver ions move from a solution to oxidizing groups in the polymer.

Were prepared aqueous solutions of 0.005 M, 0.0025 M, of the $AgNO_3$ and Na_2S salts. 0.25 g of polypropylene powder was dissolved in 50 ml of toluene. 5 ml of the respective aqueous salt solution in the presence of 0.01 g of sodium lauryl sulfate was mixed with 25 ml of toluen/PP solution. Every separately taken microemulsion (solution1)/toluene+PP and (solution2)/toluene+PP were treated by ultrasound for 20 minutes (0.6 cm diameter; Ti-tip; 20kHz; 60W/cm^2) at a temperature of 30^{0}C, by means of a cooling bath. Then, a microemulsion containing (solution2)/PP+toluene was slowly added dropwise to microemulsion (solution1)/PP+toluene at 30 ° C and sonicated for a certain time. The resulting dispersion containing silver nanoparticles sulfide and polypropylene was vacuum evaporated in order to remove the excess of solvent and product was poured onto a glass plate to form a polymer film at room temperature. Then, by hot pressing at a temperature of fusion of the polymer at a pressure of 10 MPa obtained nanocomposite films.

2.2 Equipment

Ultrasonic processing of materials made in the instrument Sonics Vibra mobil VCX 500.

The morphology of the nanocomposite and distribution of nanoparticles of silver sulfide in the polymer matrix was studied by atomic force microscopy AFM INTEGRA PRIMA and scanning electron microscope (JEOL JSM - 7600F).

The optical characteristics of the nanocomposite was investigated by UV spectroscopy Specord250 Plus and IR spectroscopy Varian 3600 FT-IR.

3. Results and Discussion

Samples of the nanocomposites were studied by scanning electron microscopy (SEM, JEOL JSM 7600). Electron microscopic examination of samples of nanocomposites PP + Ag2S shows that nanocomposites have homogeneous distribution of silver sulfide nanoparticles in polypropylene matrix.

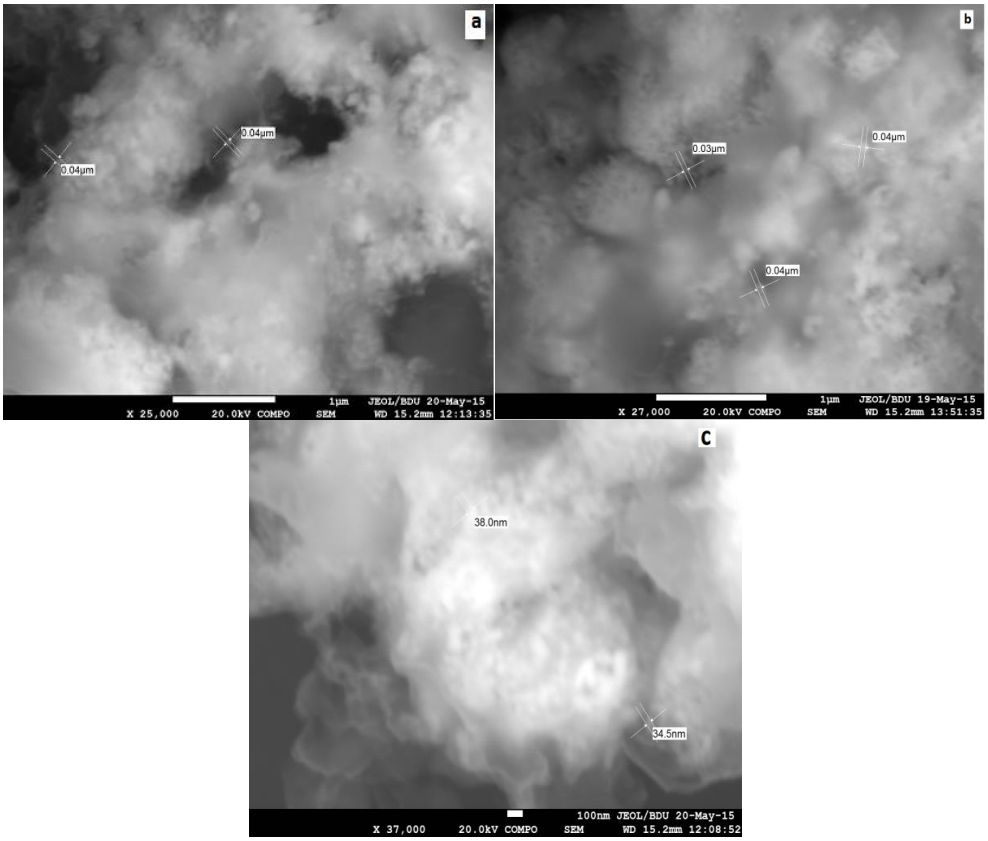

Fig.1. Electron microscope image of nanocomposites based on PP + Ag2S at various doses γ irradiation of polypropylene powders a) 15kGy, b) 30 kGy, c) 50 kGy

Fig. 1 shows an electron-microscopic images of nanocomposites based on PP + Ag2S obtained at various doses γ irradiation of polypropylene powder. As it seen, after treatment in the air of the polypropylene powders the content of Ag_2S nanoparticles in the polymer matrix increases. Electron microscopic study of nanocomposite Ag_2S in polypropylene revealed that the concentration of Ag_2S nanoparticles changes, depending on the dose of γ rays irradiation of polypropylene. It is found that the size of the nanoparticles at doses 15kGy, 30 kGy, 50 kGy is not changed, i.e. size of the Ag_2S nanoparticles is 30-40 nm.

Figure 2 shows the AFM image of the surface nanocomposites PP + Ag2S, prepared using untreated PP powder and treated with various doses of γ radiation.

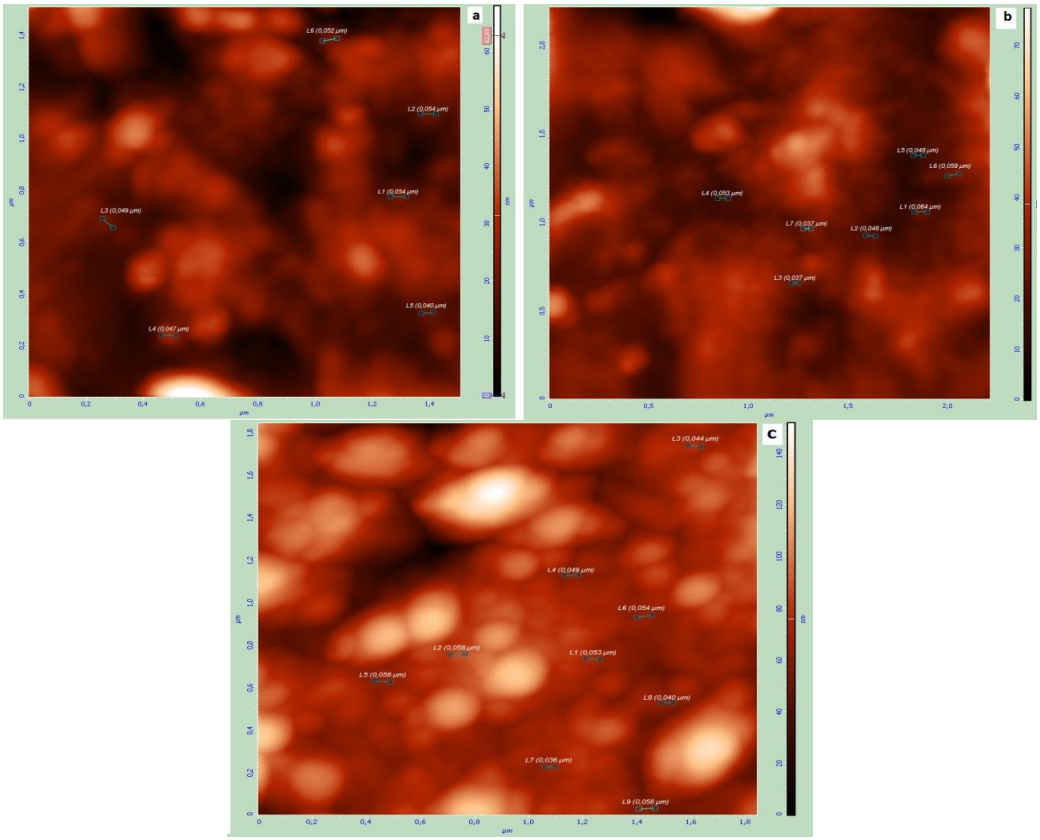

Fig. 2. Electron microscopic image of PP+Ag_2S nanocomposites at various doses of γ irradiation of polypropylene powders a) 15kGy, b) 30 kGy, c) 50 kGy

As seen, the content of Ag_2S nanoparticles in polymer matrix varies after γ-rays treatment in the air of polypropylene powder at different doses. AFM study shows that with increasing radiation dose the concentration of the nanoparticles in the polymer matrix Ag_2S increases. These experimental results correlate well with the results obtained by SEM. AFM study shows that the size of the nanoparticles at doses 15kGy, 30 kGy, 50 kGy does not change, i.e., the sizes of Ag_2S nanoparticles are 30-50nm.

Figure 3 shows a histogram of values of image pixel of the nanocomposite PP + Ag2S obtained at various doses γ irradiation of polypropylene powder. It is found that with increasing doses of γ radiation polypropylene powders led to decreasing of surface roughness, i.e. occurs the grinding of structural elements of nanocomposite surface. With increasing of γ rays doses increases the proportion of cross-linking that leads to the destruction of the crystalline structure of polypropylene and as a sequence the delaying of the formation of supramolecular structure of polypropylene. AFM study shows that with increasing γ irradiation doses the surface of nanocomposite becomes smooth. From Figure 3 seen that when polypropylene powders treated by γ radiation doses of 15kG, 30 kGy, 50 kGy the roughness of structural elements varies 200nm, 170 nm, 100 nm, respectively. The reason for changes of the structural elements of nanocompositions depending on the γ radiation dose can be explained as follows: during γ-irradiation in polypropylene formed new traps, which serve as radicals having large electron affinity that are different from the untreated initial molecules of polypropylene matrix.

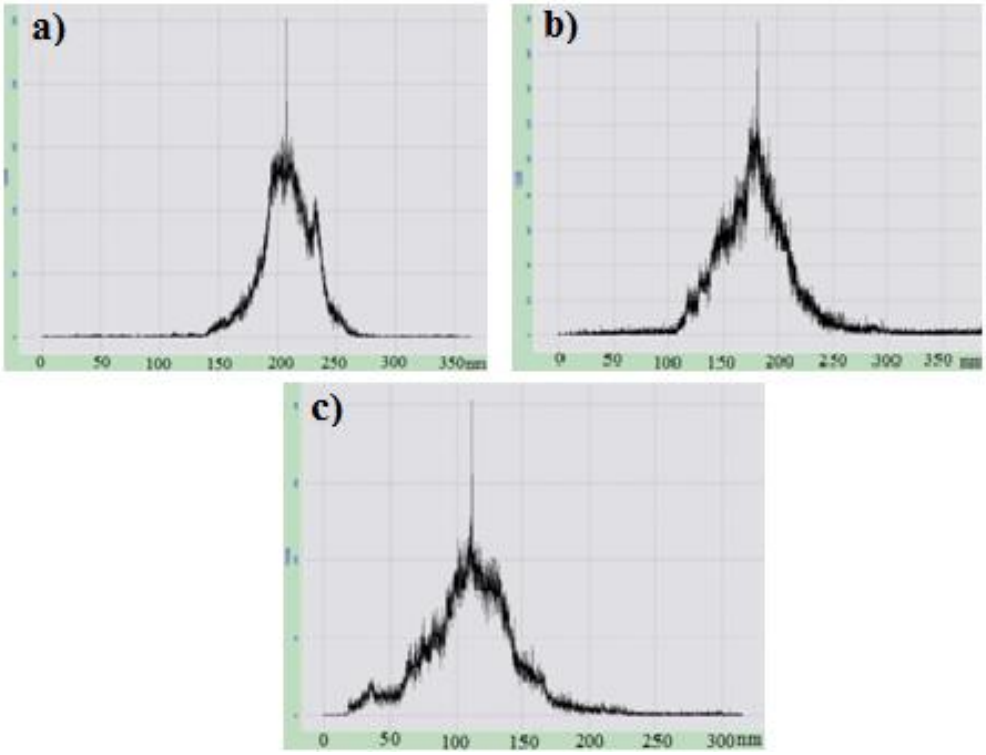

Fig. 3. Histogram of the values of elements of the nanocomposite images PP + Ag2S obtained at different γ irradiation doses of polypropylene powders: a) 15kGy, b) 30 kGy, c) 50 kGy

Polymers, having more branched structure, in which the hydrogen atoms replaced by any other group, usually subjected to destruction. First, under the influence of γ radiation the polymer molecule loses a hydrogen atom, which has excess of energy, enough to emboss the neighbouring hydrogen atom. As a result the hydrogen molecule is released, and there formed free bi-radicals. These radicals may play a role for the formation of the centre of nucleation of nanoclusters.

It should also be noted that the spatial density of polypropylene mesh (crosslinking) increases at high irradiation doses. Increasing the proportion of cross-links results in the destruction of the crystalline structure of the polypropylene. As a result there is delaying of the formation of supramolecular structure of polypropylene. Therefore, the structural elements of nanocomposite are reduced with increasing irradiation dose. This complicates their dense packing, intrinsic crystalline state, i.e., radiation breaks crystallinity.

Fig. 4 shows the IR spectra of untreated polypropylene and preliminarily irradiated one at 15 kGy in air. It was found that after γ rays irradiation the intensity of oxygen-containing groups in polypropylene significantly increased. It also shows that after irradiation the absorption band at 2360 and 2310 sm^{-1} almost disappears. After irradiation, the new bands at 1715см-1 и 1598 см-1 in the polypropylene powder appear. These peaks correspond to stretching vibration of C = O groups. The appearance of C = O groups in polypropylene is due to the oxidative processes associated with PP irradiation performed in air. Thus infrared spectroscopy showed that γ-ray treatment of polypropylene powders leads to increase of intensity of oxygenated groups in the structure of polymers. These oxygen-containing groups can play a centre of nucleation for the formation of silver sulfide nanoparticles [7].

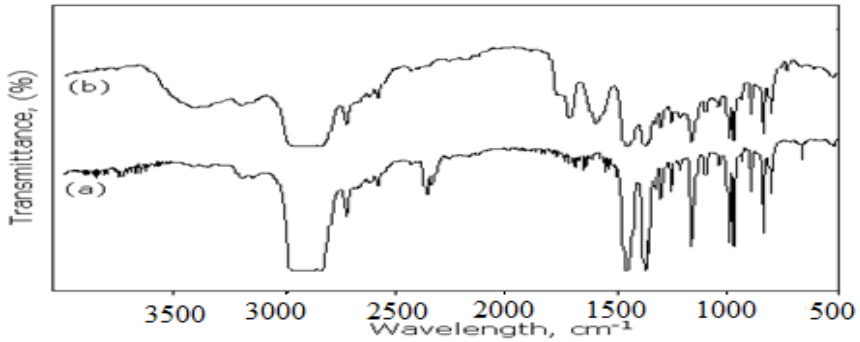

Fig. 4. IR spectrum of polypropylene (a) and pre-irradiated at 15 kGy (b)

It is also shown that γ irradiation reduces maximum of bands at 1462(CH_3,δ_a), 1378(CH_3,δ_s), 1167(C-C,ν), 997(CH_3,γ_r), 972(CH_3,γ_r), 840(CH_3,γ_r), 668 $см^{-1}$. These experimental results show that under the influence of γ-ray are destroyed C-H bonds of methyl and methylene groups, and this leads to cross-link formed radicals [8].

Figure 5 shows the IR absorption spectra of the nanocomposite PP/Ag2S obtained on the basis of pre-irradiated polypropylene powder at 15 kGy, 30 kGy, 50 kGy. It is seen that with increasing irradiation dose, the band intensity at 1715 cm-1 increases. Also, with increasing doses of irradiation, observed the increase of intensity of the band of stretching vibrations at 1083 cm -1.

To study the formation of Ag2S nanoparticles in polypropylene have been conducted the UV spectroscopic study for nanocomposites PP + Ag2S. Absorption spectra were measured with a spectrophotometer (Perkin Elmer, USA). Measurements were performed at room temperature. Figure 6 shows the UV absorption spectra of pure polypropylene nanocomposites films of PP + Ag2S obtained on the basis of γ-rays pre-irradiated polypropylene powder at 15 kGy, 30 kGy, 50 kGy.

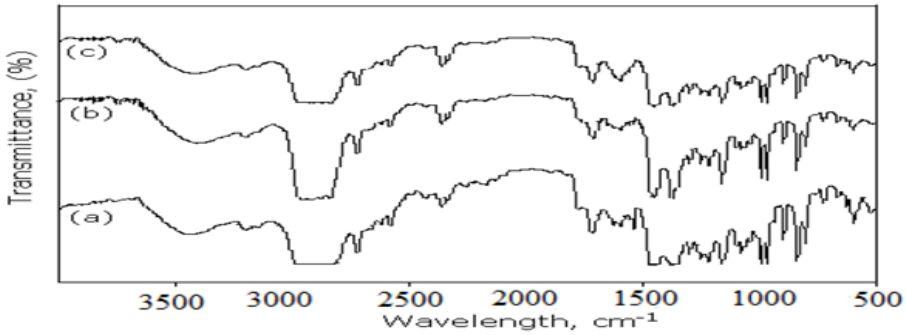

Fig. 5. IR spectra of nanocomposite PP/Ag2S prepared from previously γ rays irradiated polypropylene powders at 15 kGy, 30 kGy, 50 kGy

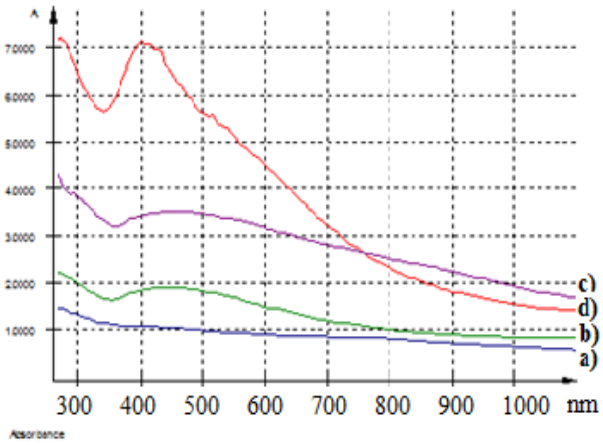

Fig.6 UV spectra of pure polypropylene film (a) and nanocomposites PP + Ag2S based on previously γ rays irradiated polypropylene powders at 15 kGy (d), 30 kGy (c), 50 kGy (b)

From figure 6 seen the absorption observed at 400 nm wavelength, and absorption intensity depends on the concentration of PP+Ag_2S. It is also found that increasing concentration of nanoparticles does not change the colour of nanocomposite i.e. the sizes of the Ag_2S nanoparticles do not changes. Was calculated the width of the forbidden zone of polypropylene and silver sulfide (see Table 1

Table 1. The bandgap (Eg) of polypropylene and silver sulfide.

Nanocomposite	**PP (eV)**	**Ag_2S (eV)**
PP (0 kGy) +Ag_2S	5,5	1,8
PP(15 kGy) +Ag_2S	2,7	1,9
PP(30 kGy) +Ag_2S	4,7	1,8
PP(50 kGy) +Ag_2S	3,4	1,6

A comparison of the band gap of silver sulfide nanoparticles and bulk crystals shows that there is a blue shift. Note that the band gap for the bulk crystal of silver sulfide varies between 0,9-1,1 eV. Increasing the width of the forbidden zone of the silver sulphide associated with a decrease in the size of the nanoparticles.

4. Conclusion

In the present work we used a combination of two synthetic methods for producing polypropylene-based nanocomposite (PP/Ag2S), by application of ultrasound and microemulsion techniques. The morphology of the nanocomposite and distribution of silver sulfide nanoparticles in the polymer matrix was studied by atomic force microscopy AFM INTEGRA PRIMA and scanning electron microscope (JEOL JSM - 7600F). Electron microscopy and atomic force microscopy study of nanocomposite showed that, depending on the γ rays dose of irradiation the concentration of Ag_2S nanoparticles in polypropylene changes. It is found that the size of the nanoparticles at 15kGy, 30 kGy, 50 kGy is not changed, i.e. size of the Ag_2S nanoparticles is 30-40 nm. It is found that with increasing doses of γ radiation polypropylene powders led to decreasing of surface roughness, i.e. occurs the grinding of structural elements of nanocomposite surface. With increasing of γ rays doses increases the proportion of cross-linking that leads to the destruction of the crystalline structure of polypropylene and as a sequence the delaying of the formation of supramolecular structure of polypropylene. Also by IR spectroscopy indicated that γ-

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