

Photoluminescence in the polymer nanocomposites on the basis of PP + CdS

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Have been stated the results of research of photoluminescent properties of nanocomposites based on polypropylene (PP) treated by discharge in air quality, which is higher than breakdown strength of air and filling compound CdS in wavelength interval $\lambda = 300-1000$ nm. Have been studied by the atomic-force microscope (AFM) the structures of nanocomposites PP + CdS samples, prepared from PP powder, treated and untreated in various intervals of time. AFM research and study of photoluminescent spectra revealed that the dimensions of CdS nanoparticles in PP did not depend on discharge treatment duration, but the concentration of CdS nanoparticles in polymeric matrix PP depended on discharge treatment duration. Has been shown the changes of CdS nanoparticles concentration in PP subject to discharge treatment duration was correlated very well with experimental data, obtained from photoluminescent spectra. It supposed that change of nanoparticles concentration subject to discharge treatment duration is connected with formation of oxidative centers in polymers, which play the role of nucleation centers for CdS.

Key words: nanocomposite, photoluminescent, polypropylene, atomic-force microscope, nanoparticle

1. Introduction

The search and preparation new photoluminescent polymeric nanocomposites (PNC) is a question of great scientific and practical importance for understanding of energy transfer mechanism, transport carriers in multiphase polymeric systems. Above-mentioned problems are important in terms of preparation luminescent screens, transducers, sensors and other facilities with improved physical-chemical characteristics and broadened intervals of phosphorescence in visible region of spectra based on such multiphase polymeric systems. Development and preparation of new photoactive nanocomposites is closely connected with understanding of interrelation “structure-technology-properties-application” of these materials. Polymeric nanocomposites, composed of two or more phases, challenge the developments of physical and chemical methods of preparation of new active elements by modification of their structures and properties [1-4]. These materials include the positive properties of polymeric matrix (flexibility, possibility to obtain the elements of any configuration and others) as well as active filler (sensitivity) and at the same time possess sufficient photoluminescent properties in combination with physical and chemical characteristics. It should be noted that by variation of components properties it is possible to change the properties of nanocomposites, to study the interface effects, to research intermolecular transfer processes and migration of electron excitation energy in polymeric medium, the influence of interface interactions on photoluminescent properties of filler [5-7]. The research of polymeric nanocomposites structures with inorganic semi-conductors (sulfides, transition metals oxides) is of interest in terms of inherent to them new electrochemical, photochemical, magnetic and other characteristics [8-10]. Structure and properties of these composites associate to each other. The data of structure (dimension and character of distribution of the particles of dispersed phase in the matrix of polymer) allow forecasting the properties of this system and vice versa the study of the properties allow forecasting the structure of nanocomposites.

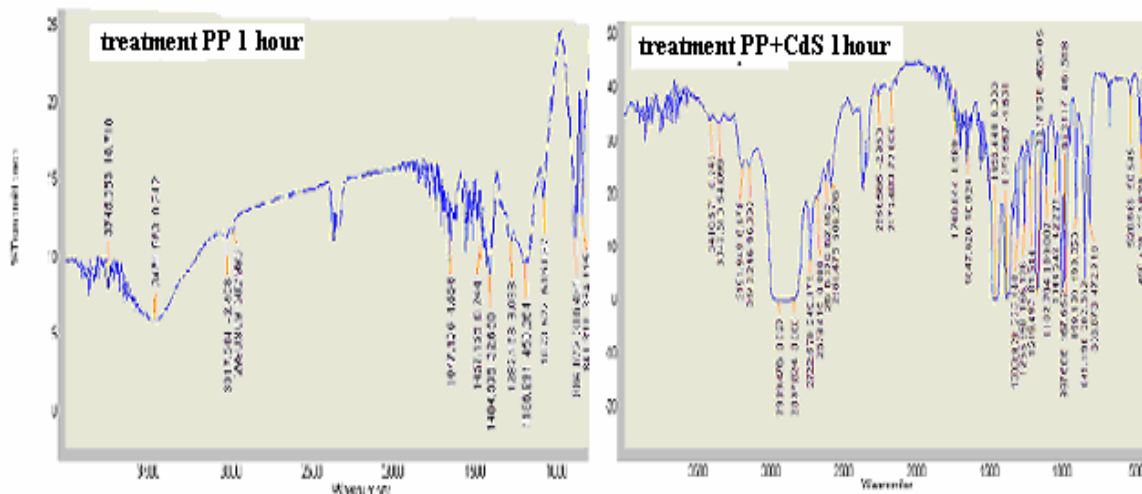
2. The Samples and experiment method

In this work is given the results of research of photoluminescent properties of nanocomposites on the basis of polypropylene (PP) and filler CdS treated in wavelength interval $\lambda = 300-1000$ nm. With aim to find out the influence of type of polymeric matrix on structure and photoluminescent properties of nanocomposites have been used the matrix differ in character of partial discharge interaction and in formation of oxidizing groups. The polymeric powder (size

of particles 0, 5-1, 0 mkm) with aim to increase the reactivity towards the transition metal ions Cd^{2+} was treated by electrical discharge in air quality, which is higher than breakdown strength of air in various intervals of time. The nanocomposite polymer + CdS was prepared by treatment of samples of powder of PP in 0,1 M solution of $CdCl_2$ and 0,1 M of Na_2S . The definite proportion of treated polymeric powders of PP first was mixing by magnetic mixer with 0,1 M solution of $CdCl_2$ during 20-25 minutes. Then filtered powder, containing Cd^{2+} ions was cleansed by water in order to remove the weakly bounded Cd^{2+} ions, and then was treated by 0,1 M solution of Na_2S . After that, the powder was getting dry in 24 hours. Further from that powder were prepared the samples of nanocomposites PP + CdS by hot-pressing method at the melting point of PP. The structural modifications of nanocomposites PP + CdS, obtained by hot-pressing method at the melting point of PP and treated in various time intervals, were studied by IR spectroscopy method. Has been studied the relief of nanocomposites samples, treated in various time intervals by electrical discharge AFM. Photoluminescent spectra have been studied on spectrofluorimeter Cary Eclipse in wavelength interval 300-1000 nm.

3. The results of experiments

The spectra, presented in Pic.1 are IR spectra of PP and nanocomposite PP + CdS samples, treated in an hour by electric discharge. It is clear from the pic.1 that there is strong change in IR spectra especially in wavelength region 2846 cm^{-1} , $1456\text{--}1186\text{ cm}^{-1}$. Depending on duration of treatment, was observed the increasing of absorption band strength in wavelength region 2950 cm^{-1} and 2846 cm^{-1} , to result from the activation of CH valence vibrations in spectra of polypropylene. It is also shown in IR spectra of nanocomposite PP + CdS samples, treated by electric discharge, the activation of absorption band strength of CH valence, deformation vibrations and vibrations mutual influence of CH and CH_2 groups were observed. It is known that interaction strength of these groups depends the degree of stereo regularity of macromolecule and rotation about C—C bonds of main chain.

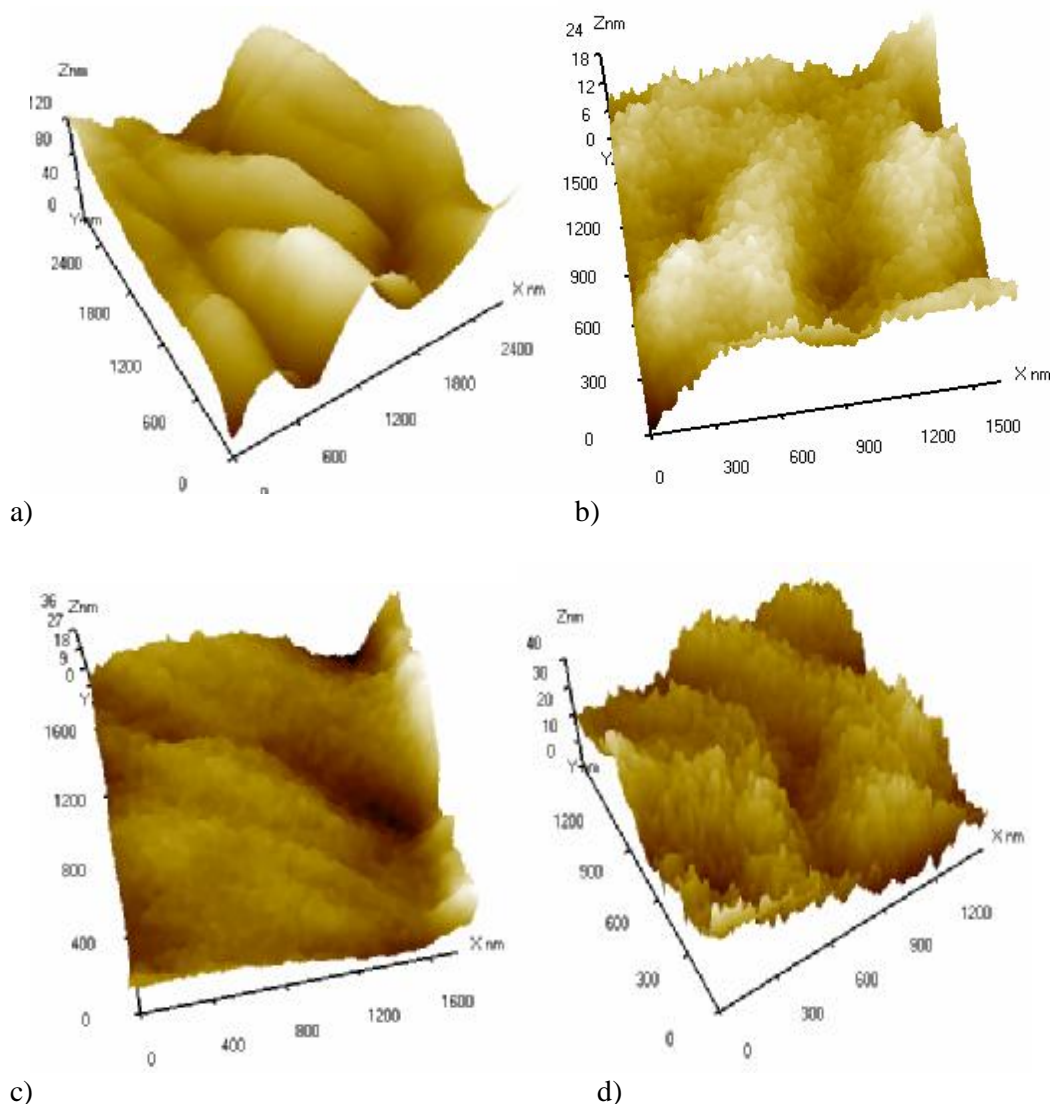


Pic.1 IR spectra of PP and nanocomposite samples, treated by electric discharge

Have been studied by the atomic-force microscope (AFM) the relief of nanocomposites PP + CdS samples, obtained from PP powder, treated and untreated by electrical discharge in air quality in 0,5 h, 1h and 3 hours (Pic.2). As it is seen in the pic.2 the relief of treated samples in various intervals of time becomes rough. The increasing of exposure time leads to increasing of concentration of CdS particles in polymeric matrix to certain extend. The formation of nanophase CdS is the result of interaction of Cd^{2+} and S^{2-} ions in the immediate volume of the polymeric matrix; they become the oxidation centers due to the discharge treatment in air quality. Cd^{2+} and S^{2-} ions move towards each other: the ions Cd^{2+} from the solution towards the oxidation groups in polymer; ions S^{2-} from solution in polymeric matrix towards the Cd^{2+} ions. To vary the concentrations of $CdCl_2$ and Na_2S it is possible to get the uniform distribution of

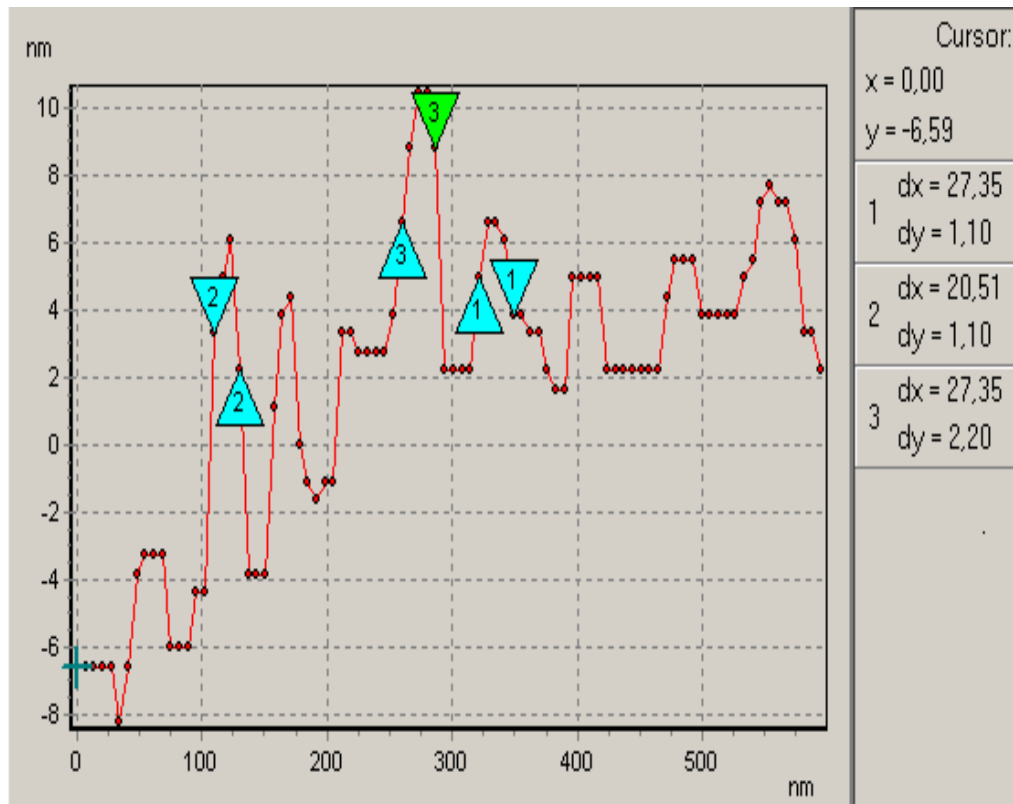
nanoparticles CdS in polymeric matrix. The usage of very low concentration of Na_2S leads to emission of Cd^{2+} ions in solution and forming CdS phase. One of the principal parameter, influencing the character of dispersed phase distribution in sample volume is the ability of polymeric matrix to form complex with transition metal ions. The ability of polymeric matrix to form complex increase with discharge treatment, i.e. the majority of dispersed component forms around the oxidation centers in polymer. The AFM-scanning of PP + CdS samples relief shows the increasing the CdS nanoparticles on the samples surface.

The dimensions of photoluminescent particles in PP matrix have been studied by scanning atom force microscope and given in pic.3. It is seen in pic.3 that the CdS nanoparticles dimension is 20-27 nm. The AFM-scanning shows the dimensions of nanoparticles do not depend the time of discharge treatment, and the concentration of CdS nanoparticles in polymeric matrix depends the duration of discharge treatment. The increasing of discharge treatment duration evidently leads to structural damage of polymer. The concentration change of CdS in PP with duration of discharge treatment seemingly is correlated with forming of oxidizing centers in polymer, which are the nuclease center for CdS.



Pic.2 3D image observed by AFM of nanocomposite PP + CdS

- a) untreated powder of PP
- b) treatment duration of PP powder 30 minutes
- c) treatment duration of PP powder 1 hour
- d) treatment duration of PP powder 3 hours



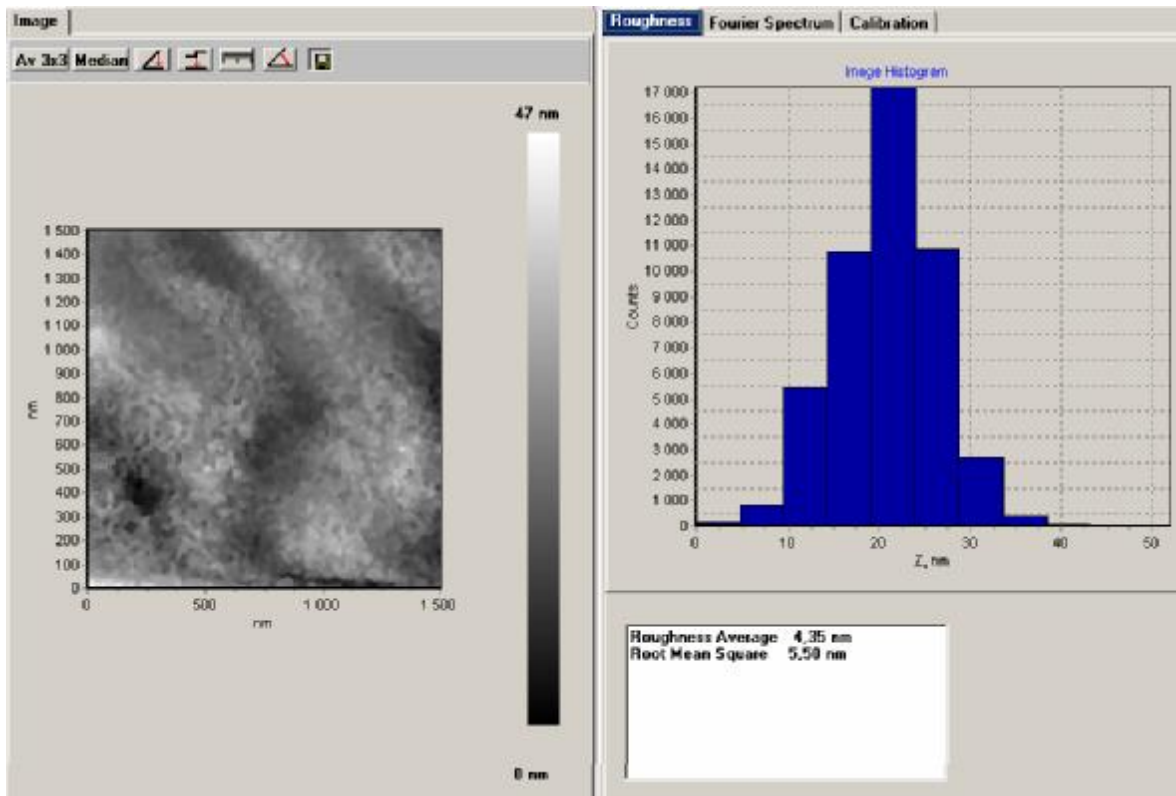
Pic.3 CdS nanoparticles dimensions in polymeric matrix

The analysis of the properties of nanocomposite PP + CdS surface and histogram of image element values is shown in pic.4. It is seen in pic.4 that root-mean-square roughness of nanocomposite surface makes 15-30 nm. Fourier analysis distribution shows that CdS nanoparticles are equally spaced in polymeric matrix.

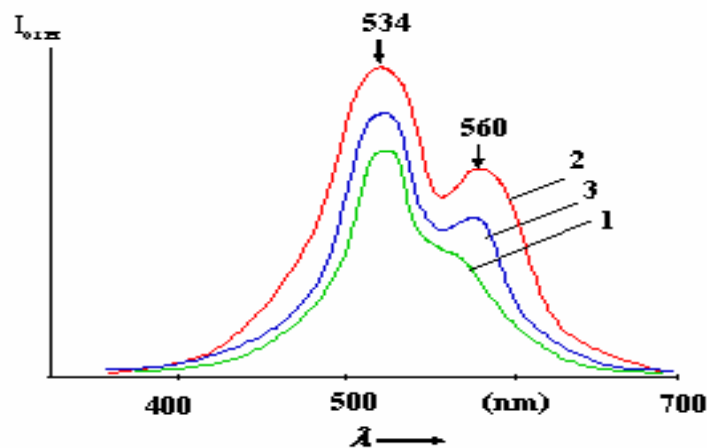
There are luminescent spectra of nanocomposite PP + CdS, prepared from polymer, treated and untreated by electrical discharge in various intervals of time in the pic.5. It is clear in pic.5 there are two maximums in wavelength interval 534 nm and 560 nm and its broadband changes with duration of treatment.

In addition, it is shown that intensity of photo fluorescence increase with discharge treatment duration of powder until 30 minutes and after that decrease.

Thus photoluminescent spectra and AFM-research reveal that scales of CdS nanoparticles in PP do not change with discharge treatment duration, and the concentration of CdS nanoparticles in polymeric matrix changes with duration of discharge treatment. The further increasing of discharge treatment duration evidently leads to damage of chemical structure of polymer. The concentration change of CdS in PP with duration of discharge treatment is correlated with experimental results, getting from photoluminescent spectra and evidently is connected with forming of oxidizing centers in polymer, which are the nuclease center for CdS formation.



Pic.4 The analysis of the properties of nanocomposite PP + CdS surface and histogram of values of element images



Pic.5 Photoluminescent spectra of nanocomposite PP + CdS, prepared from PP, treated and untreated by electrical discharge in various intervals of time.

1. $t = 0$; 2. $t = 30 \text{ min.}$; 3. $t = 3 \text{ hour}$

It is assumed, that discharge treatment of polypropylene increases the active centers in polymeric matrix, so form the traps for ions, and as result Cd^{2+} ions from solution move towards the trap, S^{2-} ions from solution move PP matrix towards the Cd^{2+} ions. The discharge treatment increases complexation ability of PP, creates optimal conditions for CdS nanoparticles formation in free volume of polymeric matrix.

In conclusion it should be noted, that mechanism of formation of nanoparticles and structure of nanocomposite with CdS in oxidized polymeric matrix along with general

characteristic has essential distinctions, caused by thermodynamical characteristics of dispersed phase and whole composition, such as heat of formation of inorganic component and surface free energy of interface of polymer-particle.

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