



Influence of heat treatment on the conductivity and radiothermoluminescence of nanocomposites LDPE - CDS obtained by the method of crazing in liquid media

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Abstract: It has been studied the temperature dependence of the resistivity of LDPE - CdS nanocomposites obtained by the crazing method of the polymer matrix in liquid medium and heat-treated in two different modes. It is shown that the observed cavity in temperature dependence of the resistivity in the samples, treated at $T = 383\text{K}$ disappears in the samples treated at $T = 413\text{K}$. 413K is premelting temperature of polymer matrix and sample structuring and disappearance of the surface porosity occurs in nanocomposites treated at this temperature due to penetration of the main part of CdS nanoparticles in the matrix volume. Changes in electrical properties of the composite after heat treatment as shows RTL spectra occurs in the result of changes in the structure of the polymer and the nature of polymer – nanoparticle interaction.

Keywords: Conductivity, Polymer, Crazing, Nanocomposite, Heat-Treatment

1. Introduction

Study of compositional nanomaterials has resulted in creation of a variety of polymer composites with semiconductor nanoparticles, which combine in themselves a high physico-mechanical characteristics of the polymer matrix and the electroactive properties of the corresponding filler [1-4]. One of the methods of nanocomposite obtain that of interest, is the formation of various types of nanoparticles in the pores pre-created in the polymer matrix by the method of their orientation extract [5]. Adjustment and stabilization of the parameters of these structures by various methods is of great interest, one of which is the heat treatment of the obtained nanostructures [6-10]. Any external influence leads to the change in the structure and electrical properties of polymers and composites based on them.

In order to study the structure of polymers and composites, it is applied a variety of methods, mechanical spectrometry, EPR, IR spectroscopy, DTA and others. The method of radiothermoluminescence (RTL) is also successfully applied together with these methods. RTL allows us to study the changes in the molecular mobility of structural elements of polymer matrix, which play a role in relaxation processes. Stability of the properties of polymer composites is

determined by relaxation processes occurring during heating of the sample, associated with molecular mobility, and also including movement of individual large and small kinetic units of polymers. In this regard, from the practical point of view it is interesting to study the influence of heat treatment and filler on the relaxation processes and the electrical properties of the composites. RTL curve of the polymer is a series of emission peaks resulting from recombination of stabilized charges within irradiation process at low temperature and state of emission peaks (RTL peaks) is closely related to the state of amorphous regions of the polymer, in particular to the position of relaxation and phase transitions [11-14].

In this regard, the aim of the work is to study changes in the electrical properties of the original and heat-treated nanocomposites obtained by orientational extraction based on low density polyethylene (LDPE) (thickness 50 mm) and nanoparticles CdS to create them crazed structure and further formation in these crazes CdS nanoparticles by chemisorption. Herewith for determining the structural changes in the composite it has been conducted radiothermoluminescence (RTL) study of the obtained

structures.

2. Experimental

The object of the study was an industrial film of low density polyethylene (LDPE) (thickness 50 mm). For creating a nanoporous structure it has been made uniaxial orientation extractor of spade cut polymer films in adsorption-active liquid medium (AAM). Orientational extraction mode for generation of the optimal porous structure has been determined experimentally and within the sorption of ions is ~ 50-60% of the original length of the polymer film. Subsequently, by the method of layered chemisorption in these pores it is formed nanoparticles of various compounds depending on the purpose of the obtained composite.

In this paper, in the pores of the pre-oriented polymer matrix LDPE it has been formed CdS nanoparticles by layered chemisorption method. Within the formation process of nanoparticles it has been produced alternately sorption in the pores of the polymer of cadmium ions Cd^{2+} and sulfur S^{2-} . It resulted in the completion of one cycle of the formation of nanoparticles. Each time after the sorption of ions the films should be washed with distilled water. Changing the number and time of the cycles of the sorption the size and amount of the nanoparticles formed in the pores of the polymer matrix can be adjusted. Formation of CdS nanoparticles in polymeric matrix has been determined by color changes of the polymer film after each cycle of formation. It has been determined the composite samples with four cycles of formation. The change of the surface resistivity ρ_s has been measured with teraohmmeter E6-13A at heating rate of 2,50K / min. Metal electrodes of planar type were placed on the surface of the sample parallel to each other and the ratio of interelectrode gap to their length was 1:10, which ensured the reliability of measurements. Measurement of volume resistivity ρ_v has been carried out in the samples in the form of a "sandwich" with a pinch of aluminum electrodes. Thermoluminescence studies were carried out on the installation TLG-69M, at a heating rate of 10 K / min and at the temperature range from 77 to 273 K. Reproducibility of the position of maxima of the RTL spectra, as a rule, was ± 2 degrees. Luminescence of the sample registered in the range of 300-820 nm by photomultiplier FEU-51, was converted into electrical signal, and then recorded on electronic tape recorder. The sample temperature was recorded with copper-constantan thermocouple.

Samples were irradiated at 77 K in pre-evacuated (at ~ 1,33·10⁻³ Pa) ampoules by γ -radiation Co^{60} source on the installation RHM - γ -25.

3. Discussion of Results

As mentioned above, it has been studied the temperature dependence of the surface resistivity ρ_s for LDPE-CdS composites thermally treated at two different modes. The measurement of each sample was performed three times. Immediately after the first heating-cooling (curve 1) with a

break ~ 30 minutes it was performed reheat (curve 2) and the third heating was performed in a day (curve 3). In order to preserve the structure of the composite the first two heating were conducted up to temperature of 413K and for the third time the sample was heated up to 453 K.

Fig.1. shows the temperature dependence of the surface resistivity ρ_s of LDPE-CdS composites thermally treated at the temperature of ~ 383K for 30 minutes.

It is seen that in all three curves at the temperature range of 293-353K there is a decline with further increase in the value of ρ_s . We think that such dependence course is the result of the porosity of the surface structure of the obtained samples within orientational extraction in liquid medium.

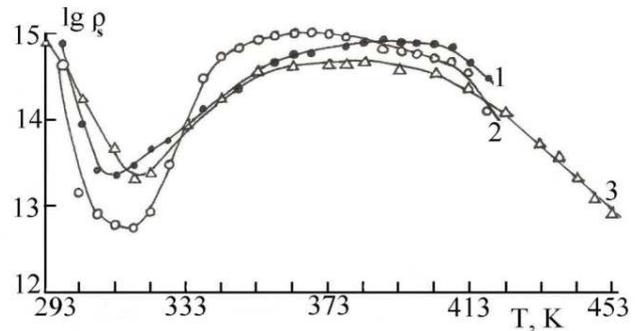


Fig. 1. Temperature dependence of the surface resistivity ρ_s for thermally treated LDPE-CdS composites: a- $T_{pr} = 383K$; 1 - first heating; 2- second heating; 3- third heating in a day.

Thus within the formation the nanoparticles of CdS formed on crazes of the polymer matrix, do not contact with each other and water molecules are accumulated in interparticle pores. During heat treatment, water desorption occurs and simultaneously the sample shrinks. In further the samples stored in the air again absorb moisture from the environment. Within the measurement of ρ_s in all three cases firstly with temperature increase it is observed the increase in conductivity through the channels consisting of adsorbed water molecules (moisture) between the nanoparticles, but the further increase in temperature leads to desorption and thus to a decrease of the conductivity of the samples. After the completion of desorption process, relatively flat portion of the dependence (350- 400 K) begins, which corresponds to the real value of ρ_s material. In this temperature range, significant changes in the structure of the matrix do not occur. After the temperature of 400-410K we observe a repeated decrease in ρ_s most likely connected with structural changes in polymer matrix under the influence of temperature, i.e., mitigation and pre-melting of polymer matrix followed by an increase in the mobility of molecular units.

Fig. 2 shows the temperature dependence of the surface resistivity ρ_s of LDPE-CdS nanocomposites thermally treated at the temperature of ~ 413K for 30 minutes.

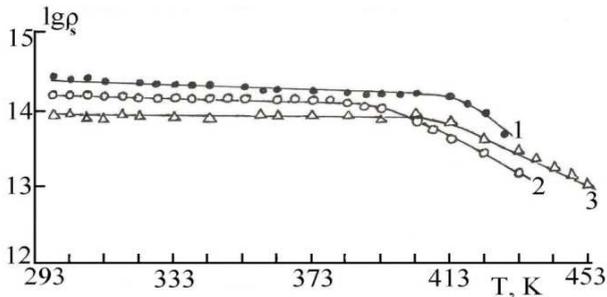


Fig. 2. Temperature dependence of the surface resistivity ρ_s for thermally treated composites LDPE-CdS: a- $T_{obr} = 413K$; 1 - first heating; 2, second heating; 3, third heating in a day

From these dependences it is seen that at heating up to to the temperature of $393 \div 403K$ the value of resistivity ρ_s of the samples remains constant within a certain error. Further heating of the nanocomposites is accompanied by decrease of the resistivity ρ_s , most likely connected with structural changes in polymer matrix under the influence of temperature. We think that the difference in the data obtained in the samples treated at two different temperatures, is the result of the influence of heat treatment mode on the structural change of LDPE-CdS nanocomposites. So $\sim 413K$ is the temperature of softening or melting of the polymer matrix and penetration occurs in nanocomposites treated at this temperature which is formed on the surface and in crazes of nanoparticles in the sample volume. And in its turn it leads to the surface structuring of the matrix and to the disappearance of the surface porosity in the result of polymer matrix encapsulating of CdS nanoparticles. Penetration into the depth of the matrix of CdS nanoparticles and disappearance of the surface porosity strongly degrades the sorption properties of the investigated LDPE-CdS nanocomposite. As a result, at dependence $\rho_s = f(T)$ the observed cavity at the temperature range of 293-353K in thermally treated LDPE-CdS nanocomposites at a temperature of about 383K is not observed in the thermally treated samples under the temperature of about 413K.

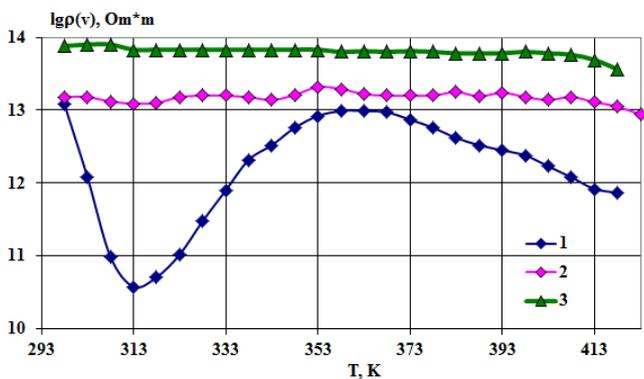


Fig. 3. Temperature dependence of volume specific resistance ρ_v of LDPE-CdS nanocomposite (4 cycles of formation) termo treated at temperature $T=383K$ (1), $T=413K$ (2) and termo pressed at temperature $T=433K$ (3).

In order to confirm the above-mentioned, the samples obtained from LDPE-CdS nanocomposites by orientational

extraction method in liquid medium, were thermally compressed and temperature variation of their volume resistivity ρ_v was studied. The results of the temperature dependence ρ_v of the heat-treated and pressed LDPE-CdS nanocomposites are presented in Fig. 3. As it is seen from the dependence, cavity is not observed in thermally pressed samples from LDPE-CdS nanocomposites as in heat-treated ones at $T = 413K$, which is seen in treated samples at 383K. In the pressed samples the semiconductor nanoparticles are mixed in the volume of polymer matrix under the influence of pressure and temperature and located in an isolated state, which greatly deteriorates the sorption properties of the obtained LDPE-CdS nanocomposite.

For determination of structural changes in the composite before and after heat treatment it has been conducted radiothermoluminescence (RTL) research of these samples. Results of these studies are reflected in RTL spectra of LDPE-CdS composites (Fig. 4). From these spectra it is seen that the peak value of the emission intensity β -relaxation maximum of the composite heat-treated at low (383K) and high temperatures (413K) are comparable, but their glow is below the emission intensity of LDPE. We consider that low-temperature processing is not sufficient for changing the structure of the composite and relatively high mobility of the polymer matrix is kept. This is confirmed by the relatively low temperature of the maximum playback ($224K \pm 2$).

After heat treatment at high temperature penetrating into the matrix volume from the sample surface, the CdS nanoparticles, interacting with macromolecules of the polymer matrix become as a structurant. As a result the crystallinity and effective interphase boundary increase, the mobility of the surface structure of the matrix with filler decreases and respectively the maximum temperature is mixed towards higher temperatures. But at the same time the expected decrease in emission intensity is not observed due to the increase in crystallinity, and we consider that it is the result of concentration growth of luminescence and recombination centers locating in interphase boundary of the polymer with the filler [11-13]. Similar changes are observed for the maximum of γ -relaxation of LDPE -CdS composites, as well.

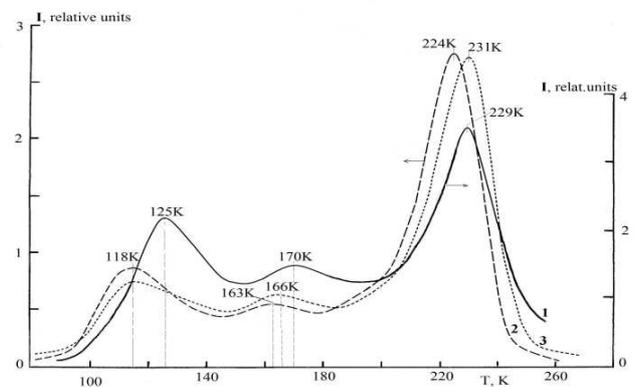


Fig. 4. RTL spectra LDPE (1) and LDPE-CdS nanocomposite (4 cycles of formation) termo treated at temperature $T=383K$ (2), $T=413K$ (3).

4. Conclusion

Thus, on the basis of the obtained data it can be said that changes in heat treatment mode allows to adjust the electrical properties of the polymer nanocomposites obtained by the method of orientational extraction of polymers in liquid medium with the further formation of nanoparticles in these layered chemisorption. The change of the electrical properties of heat-treated composites is the result of changes in polymer structure and the nature of the interaction between polymer - nanoparticles. It is planned to study the gas sensitivity of the created nanocomposites.

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