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INFLUENCE OF PREPARATION TECHNOLOGY - CRYSTALLISATION TEMPERATURE-TIME REGIME ON SUPRAMOLECULAR STRUCTURE AND PROPERTIES OF PP/Ag_2S NANOCOMPOSITES

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Thin layers of polypropylene and silver sulphide nanoparrticles based nanocomposites PP/ Ag_2S were prepared by means of the combination of ultrasonic and microemulsion methods at three different crystallization modes: high rate cooling (50 deg/min), slow cooling (2deg/min) and liquid nitrogen cooling (2000 deg/min). The supramolecular structure, morphology of nanocomposites and the distribution of silver sulfide nanoparticles in polypropylene polymer matrix were investigated by atomic force microscope method. It has been found that Ag_2S nanoparticles were more homogeneously distributed in the PP matrix and have more ordered structure when samples prepared at nitrogen cooling mode. The luminescence and electrophysical properties of PP/Ag_2S nanocomposite depending from the crystallization temperature-time (CTT) regime have also been studied. As the result of these studies have been concluded that the optimization of the CTT mode affect on the obtaining of various supramolecular structures of nanocomposites, which in turn allows to vary their dielectric and luminescent properties.

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1. Introduction

The study of supramolecular structure of polymer nanocomposite (PNC) is considered to be one of the actual scientific directions at the present time. Thus, supramolecular structure is one of the main parameters affecting the physical, chemical properties material. It is possible to modify supramolecular structure by changing the CTT mode (the melting point and the storage temperature) of the polymers, to vary the crystallization centers - and thus to change the size and number of crystallites generated during cooling of the PNC sample. Increasing of the crystallization centres leads to grow crystallization rate and reduced particles' size. This leads to the grinding of the elements of the supramolecular structure, improving their uniformity, and ultimately leads to the variability of the properties of the PNC according to the stability of the structure.

It should be noted that the one of the factors that affects the supramolecular structure of PNC is the nano-sized filler. Nanoparticles with high structural activity can even at small concentrations modify the boundary layers of the polymer as well as its entire volume.

In some cases, the high percentage of the filler may have an effect on the structure and properties of the polymer, resulting in the amorphization of the matrix, the formation of a continuous structure consisting of the nanoparticles, and the increase of the number of defects [1].

It is known that the CTT mode can affect on the durability, magnetic, heat properties, physical structure of the compound, and this, in turn, changes the interphase interactions of composite's components [2-5]. In this paper, we studied the dependence of the structure and properties of polypropylene and silver sulphide based (PP/Ag_2S) nanocomposites on the crystallization temperature-time (CTT) mode.

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2. Methods and experiments

Reagents

Reagents used for research: isotactic polypropylene powder (M 250000), $AgNO_3$ - silver nitrate, Na_2S - sodium sulfide, $C_6H_5CH_3$toluene, $C_{12}H_{25}SO_4Na$–sodium lauryl (dodecyl) sulphate, H_2O - distilled water.

For obtaining of PP/Ag2S nanocomposite samples the combination of ultrasonic and microemulsion methods was used [5]. The thin layers of PNC samples were prepared at three different crystallization modes: high rate cooling (50 deg/min), slow cooling (2deg/min) and liquid nitrogen cooling (2000 deg/min).

Equipment

The morphology of nanocomposites, the distribution of silver sulfide nanoparticles in the polymer matrix were investigated by the INTEGRA PRIMA atomic force microscope (AFM). Optical properties of nanocomposites were investigated by Cary Eclipse Varian and Varian 3600 FT-IR spectrophotometry. The dielectric properties of nanocomposites were investigated on the MNDPI E7-20 immitant device.

3. Results and discussion

The surface topography of PP/Ag_2S nanocomposites with 0.01M Ag_2S content, in dependence of CTT mode was studied by the AFM method. Figs. 1 and 2 show 3D and 2D images of the surface of nanocomposite samples obtained at three modes.

From the analysis of the 2D AFM images, it is clear that the sizes of the surface-particles were changed. Thus, when comparing these images, it is seen that Ag_2S nanoparticles are more homogeneous distributed and the composite has more ordered structure when prepared at liquid nitrogen cooling crystallization mode.

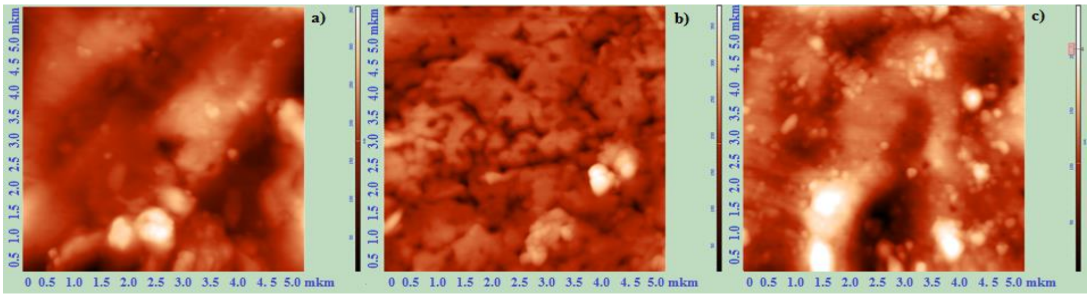

Fig. 1. 2D images of PP/Ag_2S nanocomposites samples: (a) high rate cooling (water) (50 deg/min), (b) slow cooling (2deg/min) and (c) liquid nitrogen cooling (2000 deg/min).

It is possible to explain structural changes of polymer nanocomposite samples obtained in slow-cooling mode with the growth of the elements of supramolecular structure. Thus, the growth of the spheroliths obtained at the slow cooling mode is a longer-term process than the growth of spheroliths obtained at high-rate (water) cooling mode. So, prolongation of the cooling time can cause the surface elements to grow, as well as coagulation of nanoparticles.

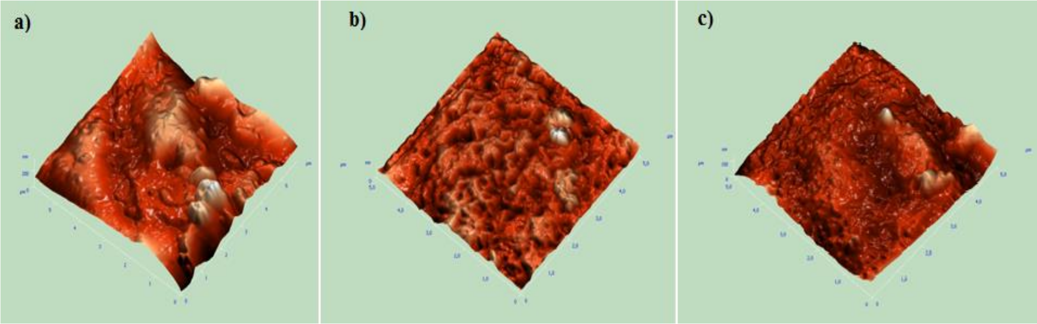

Fig. 2. 3D images of PP/Ag_2S nanocomposite samples: (a) high rate cooling (water) (50 deg/min), (b) slow cooling (2deg/min) and (c) liquid nitrogen cooling (2000 deg/min).

3D images revealed that there are some changes in the relief of nanocomposites. Thus, the relief of the sample shows that the height of the roughness decreases, and the surface structural elements are changed.

The surface density distribution (histogram) of nanoparticles in the specific area of the PP/Ag_2S nanocomposites samples depending on the CTTmode is shown in Fig. 3.

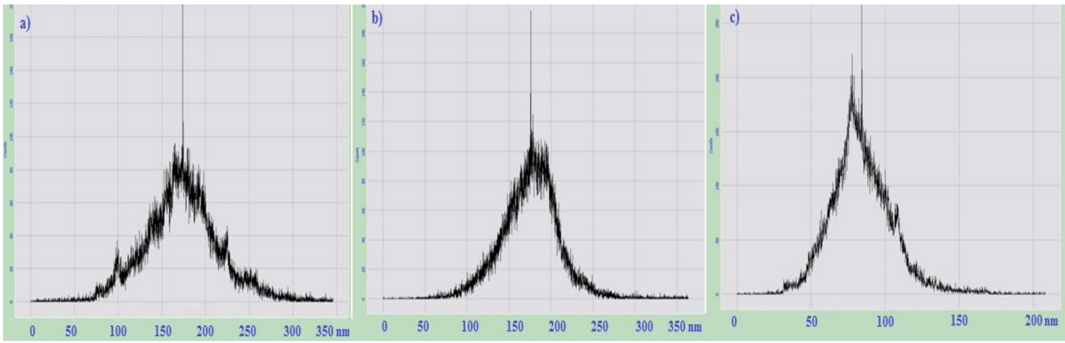

Fig. 3. The surface density distribution (histogram) of nanoparticles in the specific area of the PP/Ag_2S nanocomposites samples depending on the CTTmode: (a) high rate cooling (water) (50 deg/min), (b) slow cooling (2deg/min) and (c) liquid nitrogen cooling (2000 deg/min).

Depending on the various CTT modes, namely: high rate, slow cooling and liquid nitrogen cooling the histogram of composites with average square distribution for a certain height demonstrates the corresponding values of elements sizes: (a) 150-180 nm, (b) 160-200 nm, (c) 60-80 nm.

The highest values of the sample prepared at the slow cooling mode can be correlated with the growth of the elements of polymer matrix supramolecular structure and coagulation of nanoparticles.

The samples prepared at the liquid nitrogen cooling mode reveal the lowest value that is caused by the limitation of the growth of macromolecules when its supramolecular structure is formed at low temperatures and, consequently, reduces the roughness and grinding of surface structural elements. Also, the uniform distribution of silver sulfide nanoparticles in the polymer matrix prevents their agglomeration, causing shrink of parameter.

Structural changes of PP/Ag_2S nanocomposites samples depending on CTT mode were investigated by IR spectroscopy (Fig. 4). Measurements were taken at ambient temperature and the thickness of the samples layer was around 80 mkm.

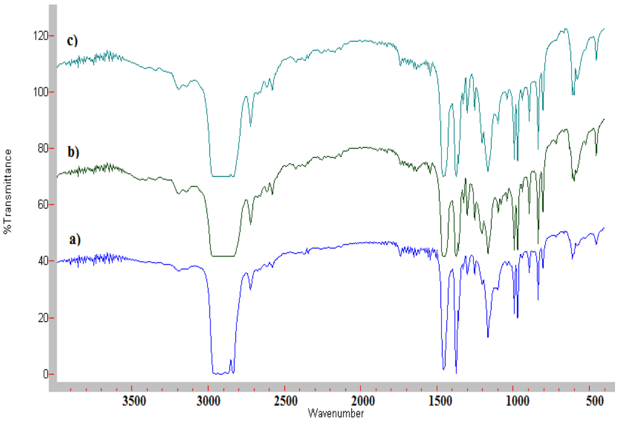

Fig. 4. IR spectra of PP/Ag_2S nanocomposites at different CTT modes: a) high rate cooling (water) (50 deg/min), b) slow cooling (2deg/min) and c) liquid nitrogen cooling (2000 deg/min).

In IR spectra of the PP/Ag_2S nanocomposites were observed the characteristic bands of the functional groups of the initial components, as well as the changes of bands intensities and shift of some bands in the samples prepared at different CTT modes.

In all three spectra of the nanocomposite samples prepared at three CTT mode were observed 1167(C-C,ν), 997(CH_3,γ_r), 972(CH_3,γ_r) cm^{-1} absorbing bands corresponding to PP's regular structure. This fact indicates that when the PP is dissolved and melted at temperatures below 180° C, the structure of polymer not affected in the nanocomposite material.

The 3450 cm^{-1} band corresponded to OH group stretching vibrations was observed only in the IR spectrum of PNC sample obtained at slow cooling mode, and was not in other samples spectra. The band corresponded to S—O symmetrical stretching reveals at 1044 cm^{-1} is not observed in the samples prepared at high rate cooling mode.

At the far ultraviolet area, was observed 602 cm^{-1} band corresponding to symmetric deformation vibrations of O-S-O group. These bands slightly shift at the 616cm^{-1} areas in the spectre of sample obtained at high rate cooling mode.

As the nanoparticles have great chemical activity, the interaction between the composite components must affect the luminescence properties of nanocomposites. The dependence of luminescence properties of the PP/Ag_2S nanocomposite samples from the CTT mode have also been studied. Figure 5 shows the luminescence spectra of nanocomposites obtained in three modes. The spectra were taken at the radiation wavelength λ_{ex} = 235 nm. In the spectra the intensities of maximum at 500, 528, 542 nm were changed.

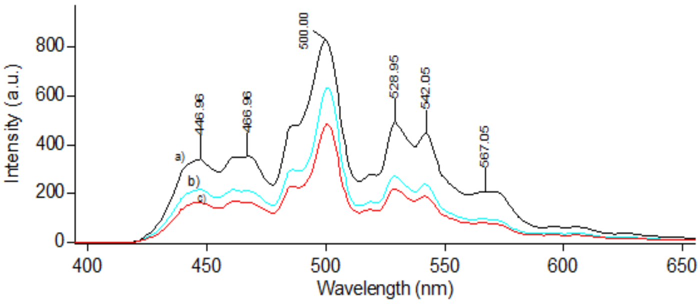

Fig. 5. Luminescence spectra of PP/Ag_2S nanocomposites obtained in different CTT modes: (a) liquid nitrogen cooling (2000 deg/min), (b)high rate cooling (water) (50 deg/min) and (c) slow cooling (2deg/min)

The highest intensity of the luminescence spectrum of the sample obtained in liquid nitrogen cooling mode can be related with the small size of the crystallites formed in the matrix and the activation of luminescent centers of the Ag_2S nanoparticles due to their increased interaction with polymer crystallites.

Thus, due to the increased interaction between nanoparticles and polymer, the centers of luminescence are activated in the semiconductor nanoparticles, which, in turn, led to growth the intensity of luminescence. In slow cooling mode, in the nanocomposites form the regions of supramolecular structure with large elements that leads to a weekened interactions between nanoparticles and polymer molecules, and causes the diminish of active luminescence centers and reduce intensity.

Have been studied the electrophysical properties of PP/Ag_2S nanocomposites with constant concentration of filler obtained at different CTT modes. The frequency dependence graphs of the PNC dielectric permeability are shown in Fig. 6. The dielectric permeability of PP/Ag_2S nanocomposites was recorded at room temperature at 10^2-10^6Hz frequencies.

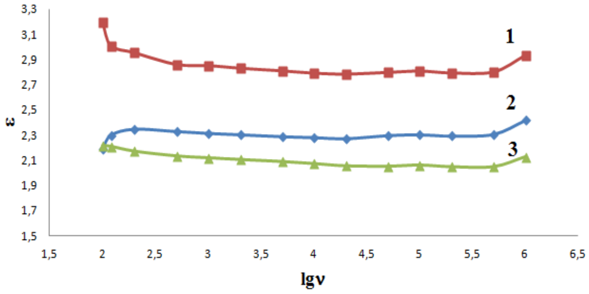

Fig. 6. The frequency dependence graphs of dielectric permeability of the PNC obtained at different CTT modes : (a) slow cooling (2deg/min), (b) liquid nitrogen cooling (2000 deg/min), (c) high rate cooling (water) (50 deg/min).

As can be seen from the graphs, the highest value of dielectric permeability has the sample obtained at slow cooling mode. The increase of dielectric permeability can be explained by the prolonged time of growth of spheroliths forming the supramolecular structure of PNC at slow cooling mode. At this cooling mode, the packing density increases that led to increasing of nanocomposite' density. Presumably all of these listed factors lead to an increase of dielectric permeability.

The decline of the dielectric permeability of the PNM sample obtained at liquid nitrogen cooling mode compared with the sample obtained at slow-cooled mode may be explained by the ion-migration polarization in nanocomposite. Thus, the possibility of defects growth in the composite obtained at the liquid nitrogen cooling mode increases.

Certain distortions in nanocomposites prepared at different CTT modes can be caused by the interactions between the PP matrix and the filler Ag_2S nanoparticles. Thus, the filler may change the crystallization kinetics of the polymer by reducing its coherence. Due to the change of the motion mechanism of the filler, the ordered parts of polymer can be dispersed by adsorption on the surface of solid particles that are the crystallization centers, and such regular parts can be dispersed at the melting temperature of the polymer.

4. Conclusion

As a result of the researches, we came to conclusion that the optimal choose of the CTT mode can have a positive impact on the supramolecular structure of PNC, the dielectric and luminescent properties of the samples. It was found out that, in the polymer matrix, the Ag_2S nanoparticles were more homogeneously distributed and regularly structured at the liquid nitrogen cooling mode.

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