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STRUCTURE AND DIELECTRIC PROPERTIES OF NANOCOMPOSITES BASED ON ISOTACTIC POLYPROPYLENE AND TITANIUM NANOPARTICLES

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In this paper we report of obtaining novel nanocomposite structures based on isotactic polypropylene and nanoparticles of titanium. The distribution of titanium nanoparticles in the polymer matrix was studied by optical (Zeiss Axio Imager A2m) and scanning electron microscopy (SEM, Jeol JSM-767F). The IR spectra reveal that after the introduction of titanium nanoparticles in the polypropylene matrix there is a significant decrease in the intensity of the band at 2950 cm^{-1} and 2839 cm^{-1} which indicate on weakening CH stretching vibrations in the spectrum of polypropylene. SEM studies of polypropylene (PP) and nanocomposites based on PP+Ti showed that the introduction of nanoparticles in polypropylene leads to change of the supramolecular structure of the polymer and forming of a relatively ordered structure with the introduction of 1% of titanium nanoparticles in the polymer. It has been also shown that the dielectric permittivity of the nanocomposite not changed as the frequency increases, and this is explained by lack of polarization processes. It was found that the temperature dependence of the resistivity of the nanocomposite has three areas. On the first and third areas the resistivity of the nanocomposite decreases linearly with temperature, on the second - decreases abruptly. The first area of depending of ρ on the temperature is conditioned by the increase of the electrical conductivity of the nanoparticles. At reaching the melting point of the polymer, due to the transition from the crystalline to the amorphous phase, the volume of the nanocomposite sample increases dramatically at a narrow temperature range, which leads to an abrupt increase in resistivity. The third area corresponds to a sharp increase of conductivity of the polymer matrix.

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Keywords: nanocomposites, polypropylene, titanium, nanoparticles, permittivity

1. Introduction

In recent years, the number of researches devoted to engineering of materials with special and practically important physical properties based on polymer composites containing metals nanoparticles significantly increased. There are complex of methods allowing to form nanoparticles in a polymer matrix [1-3]. Such metal-polymer nanocomposites have interesting properties and can find its application in various fields of technology [4-5]. It was found that the permittivity of polymeric composite material, containing metal nanoparticles is sufficiently high, to enable the use of such materials in electronics and microwave technology [2]. These systems are considered to be heterogeneous in order to study the electrical properties and use different ratios within theory of the effective medium, describing their behaviour based on the permittivity and electrical conductivity of components [6-7]. Electrical characteristics of nanocomposites metal/insulator associated with the volume fraction of the conductive filler, size and shape of the particles, as well as other factors such as adhesion between the particles and the matrix and other possible interactions between the conductive and nonconductive phases [8].

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In this paper we study the structure and dielectric properties of the metal/polymer nanocomposite based on isotactic polypropylene and titanium nanoparticles.

2. Experimental part and methods

The isotactic polypropylene (PP brand Sigma Aldrich Pcode 1001326963) has a density of 0,9 g / ml at 250C, refractive index- n20/D 1.49, transition temp - Tg -26 ° C, mol wt - average Mw ~ 250000 by GPC, autoignition temp -> 674 ° F, mp - 1890S. Nanoparticles of titanium were obtained by electroexplosive technology [2].

Polymer nanocomposites were prepared as follows: isotactic polypropylene was solved in toluene at a temperature of 120^0C. Nanoparticles of titanium added to the polymer solution at (the volume content of titanium1%, 3%, 5%, 7%, 10% in solution) and stirred for an hour to obtain a homogeneous mixture. The mixture was transferred to a Petri dish and dried in a vacuum oven in 24 hour. The thin film nanocomposite were obtained by hot pressing at the melting temperature of polypropylene and a pressure of 10 MPa. Cooling the film after hot pressing was carried out in water and the cooling rate was 200 degree/min.

Nanocomposite structure was studied by IR spectroscopy performed on Varian 3600 FT-IR. The spectrum was taken in the range of 4000 - 400 cm^{-1} at ambient temperature.

The microstructure of nanocomposites samples was studied on an optical microscope Axio Zeiss Imager A2m.

The distribution of titanium nanoparticles of in the the polymer matrix were investigated by scanning electron microscopy (SEM, Jeol JSM-767 F). Scanning was performed in LEI mode at an accelerating voltage of 15 keV and a working distance of 4.5 mm.

Measurement of the dielectric permittivity, dielectric loss tangent and resistivity of nanocomposites performed on LCR meter MNIPI E7-20. Using broadband E7-20 LCR meter to measure the frequency dependence of the capacitance and dielectric loss tangent at T=293 K in the frequency f = 25Hz-1MHz. Measurement of temperature dependence of dielectric permittivity was carried out at f = 1kHz using MNIPI meter E7-21. Measuring the value of resistivity depend on temperature was carried out by means of teraommetr E7-13 A.

3. Results and discussion

Fig. 1 shows the IR spectra of nanocomposites based on polypropylene with titanium nanoparticles. As seen from the figure, after the introduction of nanoparticles of titanium in the polypropylene matrix the intensity of many peaks of absorption bands of pristine PP decreases. As it seen after the introduction of titanium nanoparticles in the polypropylene matrix there is a significant decrease in the intensity of the band at 2950 cm^{-1} and 2839 cm^{-1} which indicate on weakening CH stretching vibrations in the spectrum of polypropylene. In the spectra nanocomposites PP +Ti with increasing of concentration of Ti nanoparticles observed the decreasing of intensity of the band at 1465 cm^{-1} corresponded to CH_2 deformation, as well as the band at 1376 cm^{-1} related to CH_3 symmetrical deformation.

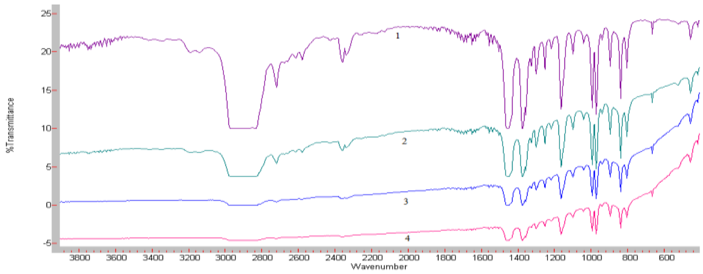

Fig. 1. FTIR spectra for the pristine PP (1), PP+1%Ti (2), PP+3%Ti (3), PP+5%Ti (4)

The surface of nanocomposites based on PP + Ti was studied by optical microscopy at various volume content of titanium (Fig. 2). It was found that the direct addition of nano powder particles at the first step in the polymer solution led to forming of the clusters that are non-homogeneously distributed in the polymeric matrix. The non-uniform distribution of the nanoparticles in a matrix of polypropylene is explained by the fact that during the mechanical mixing of the polymer with nanopowders, the nanoparticles, having high reactivity, agglomerate to each other. With increasing concentration of Ti nanoparticles the larger agglomerates formed in a matrix.

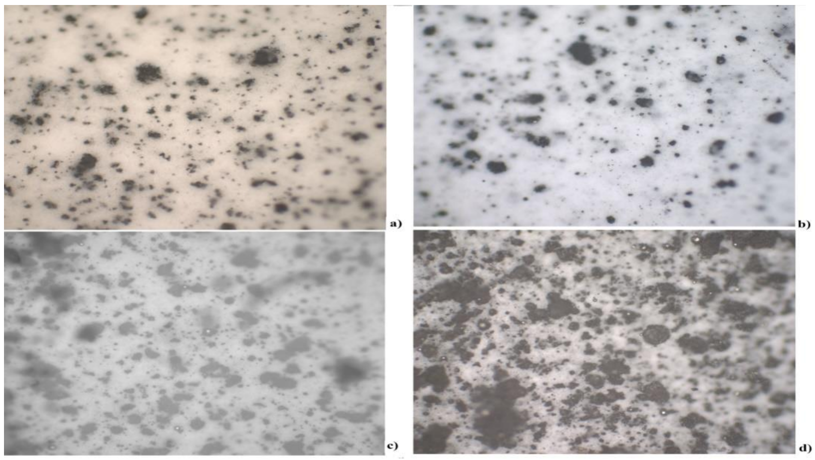

Fig. 2. The microstructure of nanocomposites based on polypropylene (PP) and titanium nanoparticles (optical range). a) PP + 0,5% Ti, b) PP + 1% Ti, c) PP + 3% Ti, d) PP + 7% Ti

Fig. 3 shows SEM images of pure polypropylene (PP) and nanocomposites based on PP+Ti. As the figure shows, the introduction of nanoparticles in polypropylene matrix changes the supramolecular structure and led to formation of nanocomposites with a relatively ordered structure. The average diameter of nanoparticles is 35-50 nm at 1% content of titanium in the polymer matrix. It is found that increasing the volume content of titanium nanoparticles led to grow the size of the nanoparticles. Thus, average diameter of nanoparticles is 30-50 nm at 1% volume content of titanium nanoparticles, whereas at 10% the sizes increase up to 45-70 nm.

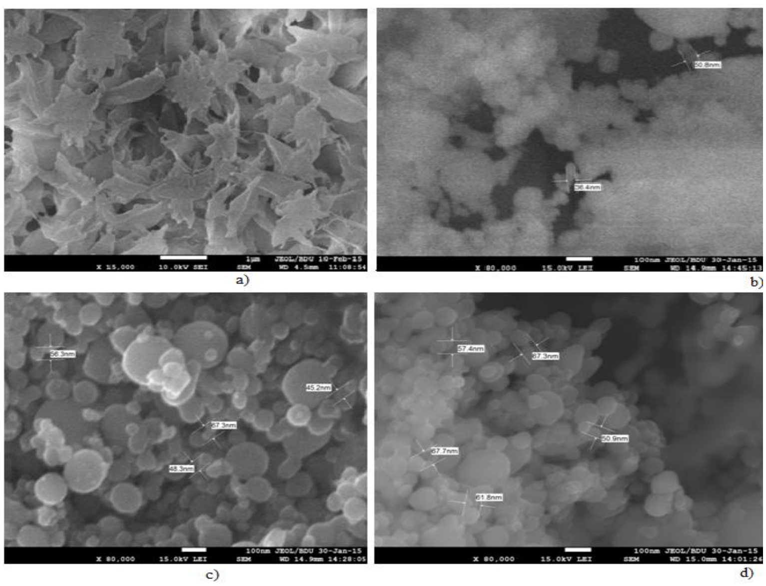

Fig. 3. SEM image PP and polymer-based nanocomposites PP(a), PP+1%Ti (b), PP+5%Ti (c), PP+10%Ti(d).

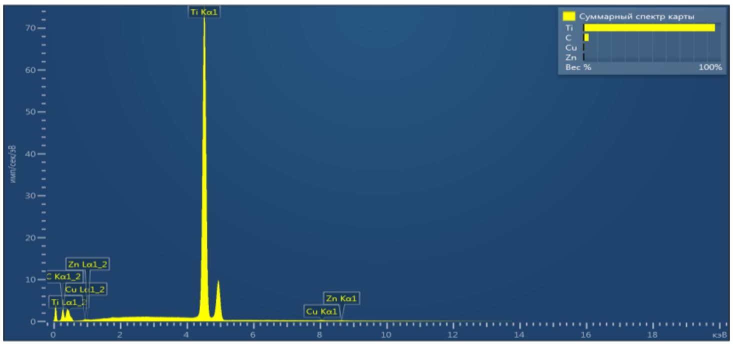

Figure 4. Energy dispersive spectrum (EDS) of nanocomposites PP+Ti.

The points, identified in the EDS spectrum Fig. 4, demonstrate the presence of Ti as the main element of the sample. The other peaks are corresponding to Cu, C being characteristic of the carbon-coated grid.

Has been studied the dependence of the dielectric permittivity of nanocomposites PP + Ti in depending on the frequency. Fig. 5 shows the dependence of the dielectric permittivity of nanocomposites on the frequency.

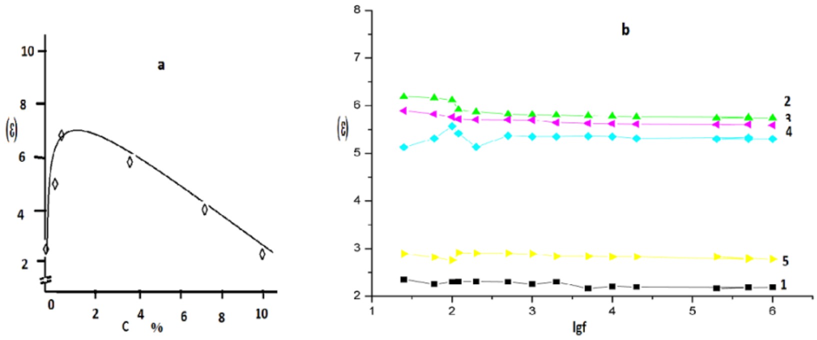

Fig. 5. The dependence of the dielectric permittivity of nanocomposites on concentration of titanium nanoparticles (a) and frequency (b).
1. PP, 2. PP + 1% Ti, 3. PP + 5% Ti, 4.PP + 7% Ti, 5. PP + 10% Ti

As it is seen from Fig. 5 the additions of 1% volume content of titanium nanoparticles in the dielectric matrix of polypropylene PP, the dielectric permittivity of nanocomposites increases, and then decreases. It is assumed that a 1% volume content of titanium nanoparticles act as a structurant in the matrix, and with increasing concentration the conductivity of the nanocomposite increases and thus decreases the dielectric permittivity. Also as it seen from Figure 5, the dielectric permittivity does not change with increasing of frequency. In our opinion, it is due to the fact that in this case, there are almost no polarization processes, i.e. with further increase of the nanoparticles' concentration, they behave as a separate dispersed phase and therefore the increase of their concentration led to growth of the conductivity of the compositions.

With the introduction of Ti nanoparticles into the PP decreases the dielectric loss tangent value (Fig. 6). Reducing the value of the dielectric loss with the addition of metal nanoparticles is due to the formation of the optimal structure and Ti nanoparticles act as structurant.

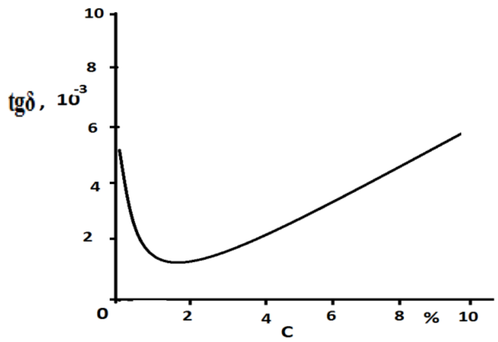

Fig. 6. The dependence of the dielectric loss tangent of the nanocomposites from titanium concentration.

Have been studied the dependence of the dielectric permittivity and the resistivity on temperature. Fig. 7 shows that increasing concentration of titanium nanoparticles up to 1%, the value of dielectric permittivity increased, but further increasing of concentration reduces the dielectric permittivity. With increasing concentration of the titanium bulk density of defects in the polymer matrix increases. Up to 1% volume content of nanoparticles in polypropylene, they act as structurant, and as a result formed a relatively ordered structure of nanocomposites. It also shows that the increasing of temperature not too much influence on the dielectric permittivity.

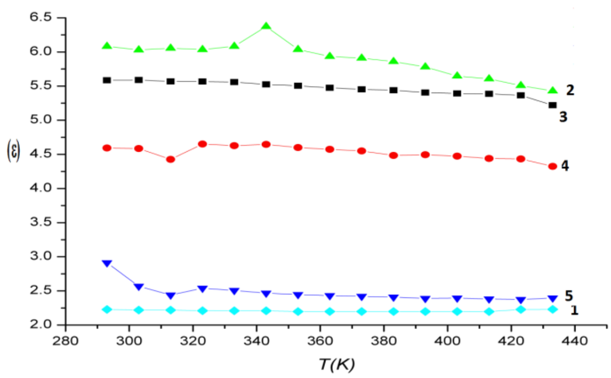

Fig. 7. The dependence of the dielectric permittivity (ε) of the nanocomposites from temperature.
1 PP, 2.PP+1%Ti, 3.PP+5%Ti, 4.PP+7%Ti, 5.PP+10%Ti

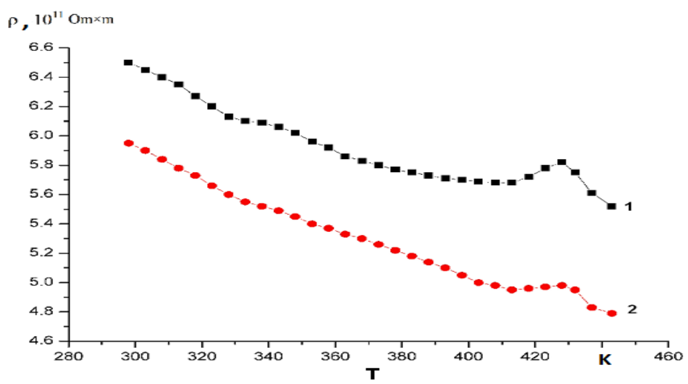

Fig. 8. The dependence of resistivity of nanocomposites on temperature.
1. ПП+0,5%Ti; 2. ПП+7%Ti

It is shown on Figure 8 that the resistivity decreases gradually with increasing of temperature up to 420K, then there is a slight increase in resistivity at 430K, and further increase of temperature leads to an abrupt decrease in resistivity. Also from Fig. 8 seen that the value of ρ_v for PP + 0.5%Ti is greater than for PP + 7%Ti nanocomposites. We see that the temperature dependence of the nanocomposite' resistivity has three area. In the first and third area nanocomposite resistivity decreases linearly with increasing of temperature, at second area it decreases abruptly. The first area of depending of ρ on the temperature is conditioned by the increase of the electrical conductivity of the nanoparticles. At reaching the melting point of the polymer, due to the transition from the crystalline to the amorphous phase, the volume of the nanocomposite sample increases dramatically at a narrow temperature range, which leads to an abrupt increase in resistivity. When the destroying of crystalline phase of the polymer, the average distance between the titanium nanoparticles increase. Most probably here nanoparticles are the source and collectors of electrons in jumping mechanism of charge transfer and consequently should decrease the electrical conductivity of nanocomposite. The third area corresponds to a sharp increase of conductivity of the polymer matrix.

4. Conclusion

As is seen from IR spectra of nanocomposites on the basis of polypropylene with Ti nanoparticles PP+Ti, the introduction of titanium nanoparticles in polypropylene matrix results the significant decrease of intensity of the band at 2950 cm^{-1} and 2839 cm^{-1} which indicate on weakening CH stretching vibrations in the spectrum of polypropylene. SEM studies of polypropylene (PP) and nanocomposites based on PP + Ti showed that the introduction of nanoparticles in polypropylene leads to change of the supramolecular structure of the polymer and forming of a relatively ordered structure with the introduction of 1% of titanium nanoparticles in the polymer. It has been also shown that the dielectric permittivity of the nanocomposite not changed as the frequency increases, and this is explained by lack of polarization processes. It was found that the temperature dependence of the resistivity of the nanocomposite has three areas. On the first and third areas the resistivity of the nanocomposite decreases linearly with temperature, on the second - decreases abruptly. The first area of depending of ρ on the temperature is conditioned by the increase of the electrical conductivity of the nanoparticles. At reaching the melting point of the polymer, due to the transition from the crystalline to the amorphous phase, the volume of the nanocomposite sample increases dramatically at a narrow temperature range, which leads to an abrupt increase in resistivity. The third area corresponds to a sharp increase of conductivity of the polymer matrix.

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