

CHANGE IN THE PROPERTIES OF POLYMER NANOCOMPOSITES (PP+ZrO₂) WITH METAL OXIDE NANOADDITIVES AFTER ELECTROTHERMOPOLARIZATION

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The presented scientific article discusses the changes taking place in isotactic propylene and metal nanoadditive nanocomposite before and after exposure to ETP. Depending on the percentage of the metal nanoadditive in the PP+ZrO₂ nanocomposite, the permittivity (ϵ), dielectric loss angle ($\text{tg}\alpha$), and logarithm of resistivity ($\lg\rho$) are observed. The obtained dependence is explained by the high permittivity of the nanoadditive incorporated into the polymer matrix. Also, the incorporation of the nanoadditive leads to the formation of structural defects and, as a consequence, an increase in electrical conductivity and a decrease in strength. The change in the dielectric properties of the PP+3% ZrO₂ nanocomposite before and after electrothermopolarization was determined at a constant electric field strength. TSD curves have been plotted that characterize the electret state at various values of the electric field, and the parameters of the electret state have been calculated from these curves.

Keywords: nanocomposites, polypropylene, electrothermal polarization, mechanical and electrical strength, thermally stimulated depolarization current.

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INTRODUCTION

In recent years, in connection with the development of information technologies, biotechnology, medicine, etc. interest in nanoscale systems and, accordingly, in nanocomposites has sharply increased, since these objects have a number of specific features compared to ordinary bulk materials.

Nanostructured metal-polymer materials are an interesting area of modern science and nanotechnology, since the use of metals, their oxides, or complexes leads to a change in the catalytic, optical, magnetic, and other properties of polymer materials. The study of nano- and microworld objects is a priority direction in the development of modern science and technology. In recent years, there has been increasing interest in research related to the production of metallic nanomaterials and the study of their structure and properties, which is currently one of the most urgent problems of metallurgy. However, the resulting nanocomposites are often under the influence of external factors, especially the electric field. Of particular interest are the changes that occur in these nanocomposites under the influence of the electric field. By adding additives of various nature to polyolefins, it is possible to increase or decrease the stability of their electret states. Based on a large number of experiments, it can be judged that the stability of the electret states of these substances can be controlled by introducing nanometal oxides into polymers [1-4]. One of the most important effects of the electric field is the change in charge state in these nanocomposites. And, of course, this change, like all other properties, also affects the dielectric properties. In nanocomposites under the influence of the electric field migratory polarization, a change in dielectric losses, and injection phenomena at the boundaries with electrodes can be observed.

EXPERIMENTAL PART

To obtain nanocomposites, the polymer is first dissolved in toluene at the melting point, and then ZrO₂ nanoadditive stabilized with Y₂O₃ is poured into the mixture. Nanocomposite samples with a thickness of 50-100 μm are obtained after storing the resulting nanomaterial under the suction cabinet and holding it for 3 minutes at a pressure of 15 MPa by hot pressing. Thus, in the mode of fast cooling at a rate of 20-35 $^{\circ}\text{C}/\text{sec}$, the composites were immersed in the water-ice mixture together with the foil. Polymer nanocomposites were exposed to various electric field strengths for 1 hour at a temperature $T=373\text{K}$ below the breakdown voltage of the electric field. The strength properties of the studied nanocomposites were determined at room temperature [5]. The permittivity (ϵ) and dielectric loss tangent ($\text{tg}\alpha$) were measured with an E8-4 automatic device at a frequency of $100\text{-}10^6$ Hz, and the resistivity with an E6-13A teraohmmeter. The electret state was studied starting from room temperature in the range of 20 $^{\circ}\text{C}$ -200 $^{\circ}\text{C}$ for 4 min/cm. To obtain the electret state in the polyolefins under study, the samples are placed between two electrodes in the device used. It should be noted that the surface charge density, activation energy, and thickness of the polymer matrix inside the composite, which are the main characteristics of the electret state, are studied by the method of thermally stimulated depolarization, which is one of the most effective and widely used methods. The activation energy of the nanocomposites was calculated by the Garlick-Gibson method. This activation energy value indicates that the traps formed as a result of polarization are high-energy. The thickness of the interfacial layer is calculated by the formula

$$\delta = \frac{2ne^2}{\epsilon_1\epsilon_2\kappa T}$$

Here ε_1 and ε_2 – is the permittivity of the polymer and nanoadditive, k – is the Boltzmann constant and T – is the absolute temperature.

nanocomposite samples on the percentage of nanoadditive. As is seen from the figure, with an increase in the percentage of nanoadditive, i.e. ZrO_2 nanometal oxide, the permittivity (ε) and dielectric loss angle ($tg\alpha$) values in these samples increase, however, despite this, we observe a decrease in the resistivity $lg\rho$.

RESULTS AND THEIR DISCUSSION

Figure 1 shows the dependence of the electrophysical parameters of PP+ ZrO_2

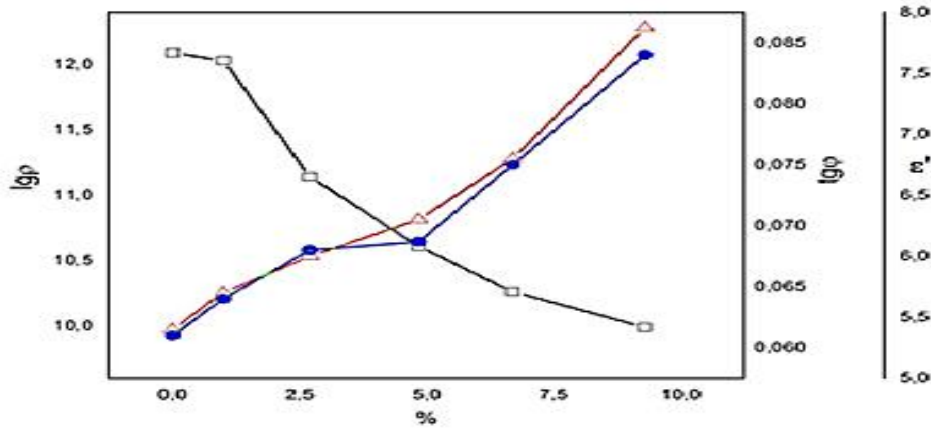


Fig. 1. Dependence of the permittivity (ε), dielectric loss angle ($tg\alpha$) and logarithm of resistivity $lg\rho$ in PP+ ZrO_2 nanocomposite on the percentage of nanoadditive

The dependence obtained can be explained by the high permittivity of the nanoadditive incorporated into the polymer matrix. Thus, if the permittivity of isotactic polypropylene, which we take as a matrix, is 2.2, the permittivity of ZrO_2 that we take as a nanoadditive is 25. In our opinion, the incorporation of metal oxide nanoadditives into the matrix leads to the formation of cracks, which reduces the resistivity of the nanocomposite. Naturally, a decrease in resistivity leads to an increase in the conductivity of the nanocomposite [6].

is a correlation between ε , $tg\alpha$ and electrical strength. For non-polar polymers, the permittivity ε is due to electron polarization, while dielectric loss is due to two reasons - dipole polarization and electrical conductivity. Changes in the molecular structure also affect these parameters [7,8]. It is noteworthy that, in our opinion, the main reason for the strength loss of the nanocomposite is an increase in conductivity. The observed decrease in strength is due to the formation of numerous structural defects, which is confirmed by the results of TSD. To study the stabilization properties of electric charges the process of depolarization of nanocomposite samples is considered [9].

Figure 2 shows the dependence of the electric strength, permittivity (ε) and loss angle tangent ($tg\alpha$) of PP+3% ZrO_2 nanocomposites on various electric field strengths. It can be seen from the figure that there

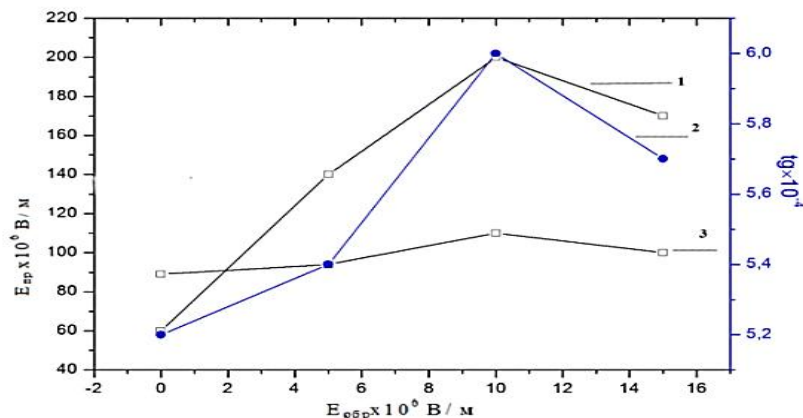


Fig. 2. Dependence of the electric strength, permittivity, and dielectric loss angle of the PP+3% ZrO_2 nanocomposite on the treatment intensity of electric field.

Figure 3 shows the TSD curves obtained after exposure to nanocomposites of various values of electric field strength. By calculating the area under the curves, the activation energy of the charges released from the traps, the thickness of the interfacial layer between the matrix and the nanoadditive, and the amount of charge per unit area can be calculated. These parameters calculated by us are given in Table

1. The maxima formed by the curves are determined by the amount of charge released from the traps. The activation energy of nanocomposites has a value of 0,72 eV at the field value $E=10 \cdot 10^6$ V/m, keeping the temperature constant. This activation energy value indicates that the traps created by polarization have high energy [10, 11].

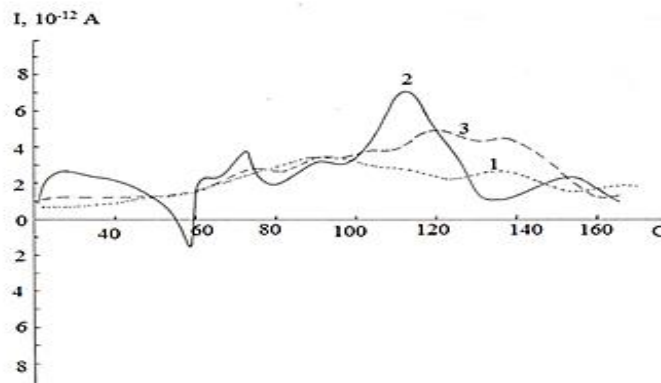


Fig. 3. TSD curves plotted after exposure of PP+3% ZrO₂ nanocomposites to ETP at various electric field strengths 1- $E=5 \cdot 10^6$ V/m, 2 $E=10 \cdot 10^6$ V/m, 3 - $E=15 \cdot 10^6$ V/m.

If we compare the calculations obtained from the TSD curves, then it can be seen that at a field value of $E=10 \cdot 10^6$ V/m, these parameters get the maximum value.

Table 1.

Surface charge density, activation energy, thickness of the interfacial layer inside the polymer matrix composite, calculated from TSD curves at different electric field strengths at a temperature of $T=373$ K.

	$E=5 \cdot 10^6$ V/m	$E=10 \cdot 10^6$ V/m	$E=15 \cdot 10^6$ V/m
$\delta(\mu\text{m})$	$7,211 \cdot 10^{-12}$	$11,4 \cdot 10^{-12}$	$11,1 \cdot 10^{-12}$
$q(\text{C/m}^2)$	$95,3 \cdot 10^{-7}$	$150,53 \cdot 10^{-7}$	$148 \cdot 10^{-7}$
$Q(\text{C})$	$4,672 \cdot 10^{-9}$	$7,37 \cdot 10^{-9}$	$7,24 \cdot 10^{-9}$
$E(\text{eV})$	0,44	0,72	0,38

CONCLUSION

Thus, after exposure of nanocomposites consisting of PP+ZrO₂ to ETP, a significant change in charge state occurs, which affects their strength and dielectric properties. The regions between the amorphous and crystalline phases play the role of

traps. In heterogeneous polymer compounds, there are boundaries that separate two phases, which in most cases act as energy traps. By varying the percentage of polymer and nanoadditive, it is possible to increase or decrease the thickness of the boundary layer, thereby controlling the electret states and dielectric properties.

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