
INFLUENCE OF ANISOMETRIC FILLERS ON ELECTRICAL PROPERTIES OF POLYPROPYLENE GLYCOL-BASED NANOCOMPOSITES

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Electrical properties of polypropylene glycol-based nanocomposites have been studied using the impedance spectroscopy method. The application of the Miyamoto-Shibayama equation enabled the contributions of the activation and nonactivation mechanisms of charge transfer in the systems filled with laponite to be separated. The critical temperature of a mechanism change was determined. Using the equivalent circuit method and the Macdonald theory, two types of conductivity, ionic and electronic, are found in nanocomposites filled with carbon nanotubes.

1. Introduction

Polymeric nanocomposites have been the objects of intensive researches within the last decade as a new class of materials [1–11]. These are novel types of functional materials with improved properties which can be used in various branches of polymer applications. The insertion of even a small amount of a filler (0.1–5 wt.%) gives rise to an improvement of polymer parameters [4–10]. To obtain designed properties, the substances consisting of inorganic nanoparticles (oxides, nitrides, carbides, silicates, and so on) are introduced into a polymeric matrix. Nanoparticles are also included into the content of nanocomposites based on various clays and polymers. An incompatibility between those inorganic and organic components is the major problem that should be overcome when creating such materials. This problem can be solved by modifying the clay with an organic substance. Modified clays (organoclays) are better combined with polymers to form layered polymer nanocomposites [2]. Organoclays have advantages over ordinary clays: they are well dispersed in a polymeric matrix [2] and interact with polymeric chains [3]. To create organoclay-based polymeric nanocomposites, natural inorganic layered structures are used, such as montmorillonite [4, 5], hectorite [3], vermiculite [6], kaolin, saponite [7], and others. In the recent years, nanocomposites were obtained with the use of laponite, a layered silicate of the

synthetic origin, which is a structural analog of montmorillonite [8, 9]. Another promising filler is carbon nanotubes (CNTs), the insertion of which into a polymeric matrix creates large opportunities for the development of new multifunctional materials with a wide spectrum of their applications in the industry [10]. By introducing nanocomposites into a polymeric matrix, the thermal stability and mechanical properties of polymers can be improved [11]. This occurs owing to the combination of properties inherent to organic (lightness, flexibility, plasticity) and inorganic (durability, thermal and chemical stability) materials [5]. However, the mechanism of influence of nanocomposites on the charge transport in and the electrical properties of polymeric nanocomposites has not been researched to the full. Therefore, this work aimed at studying the influence of organo-modified laponite (OML) and CNTs on the electrical properties of and the charge transfer in nanocomposites on a basis of polypropylene glycol (PPG). Besides the fundamental interest, the PPG-OML systems are also of applied value, because, after introducing an inorganic salt into them, they can be used in various ionic devices as nanocomposite polymeric electrolytes.

2. Experimental Part

In our study, we used nanocomposites created on the basis of polypropylene glycol and anisometric nanofillers such as organo-modified laponite and carbon nanotubes. Polypropylene glycol ($M_w = 400$, Aldrich company) was selected as a polymeric matrix. Laponite (Laponite-RD Southern Clay Products company) was used without preliminary purification. To simplify the laponite conversion to the organoform, it was preliminarily converted to the sodium form by the fivefold treatment of an aqueous mineral dispersion (0.1 mol/l) with a sodium chloride solution. Afterward, the mineral was centrifuged from the solution and washed free from sodium chloride

up to the negative reaction to the chlorine-ion with silver nitrate.

To obtain organo-modified laponite, the produced sodium laponite was treated with a stoichiometric amount of the organic salt hexadecyltrimethylammonium bromide (Merck company) for 24 h at a temperature of 75 °C. The loose deposit of hexadecyltrimethylammonium laponite was concentrated on a centrifuge and sublimation-dried to preserve its high dispersion and its ability to disperse in organic media.

Multilayered CNTs (Spetsmash corporation, Ukraine) were prepared using the chemical vapor deposition method at a mineral impurity content of 0.1 wt.%. The specific surface of CNTs was 190 m²/g, the external diameter 40 nm, and the length 5–10 μm.

Before the application, PPG was dehydrated by heating it in vacuum at 80–100 °C for 2–6 h and at a residual pressure of 300 Pa. Nanocomposites were fabricated using the ultrasonic mixing technique on an UZN-22/44 ultrasonic disperser under normal conditions. The filler content was 0.1–5 wt. %.

To detect the influence of a filler on the charge transfer processes, we studied the electrical properties of the composite using the impedance spectroscopy method with the help of a Z-2000 impedance meter. A specimen was placed between the cell electrodes, and the real, Z' , and imaginary, Z'' , parts of its impedance were measured. The measurements were carried out in the temperature interval from 0 to 40 °C and the frequency range of 1 Hz–2 MHz. The constant gap between electrodes was 0.11 mm.

3. Results and Their Discussion

The temperature dependence of the conductivity is usually described making use of the Vogel–Tammann–Fulcher (VTF) empirical equation [12]

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{B}{T - T_0}\right), \quad (1)$$

where B is the pseudo-activation energy for a given polymer, which is determined by the substance origin or, to be more exact, a free volume fraction characteristic of this polymer; T_0 is the Vogel temperature, i.e. the temperature, at which the free volume fraction equals zero; and σ_0 is the dc conductivity at $T \rightarrow T_0$.

There are two basic macroscopic models, in which the temperature dependence of the conductivity is described well by Eq. (1): the free-volume model and the configurational entropy one (Fig. 1).

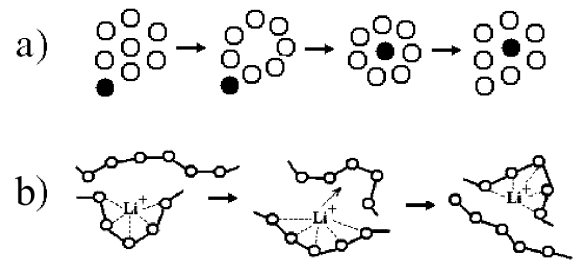


Fig. 1. Diagrammatic representations (a) of the free-volume model (here, the hollow circles stand for macromolecular segments and the solid ones for charge carriers) and (b) of the configurational entropy model, in which a Li^+ ion interacts with ether oxygen atoms of a PPG macromolecule

The free-volume model (Fig. 1,a) [12–14] is based on that the segments of a polymeric chain move only owing to a redistribution of the free volume, the motion being not a thermally activated process. The transport and relaxation processes in the system are governed by the rate of appearance of the so-called “voids” in the polymer, the dimension of which is sufficient to contain a charge carrier or a macromolecular segment. The parameter B in this model is determined by the formula

$$B = \frac{\gamma \nu^*}{\alpha \bar{\nu}_M}, \quad (2)$$

where γ is a constant that takes the possibility of free volumes to overlap into account; ν^* is the critical free volume per one mole of a monomer; α is the difference between the thermal expansion coefficients of a polymer in the vitreous and highly elastic states; and $\bar{\nu}_M$ is the average molar volume of monomer links in the temperature range from T_0 to T . Hence, the parameter B is not an activation barrier in this model; it only characterizes the ability of the polymeric matrix to form the critical free volume and to expand [13].

According to the configurational entropy model (Fig. 1,b), the transport in a polymeric system occurs through conformational changes of macromolecular chains [12–14]. If the temperature decreases, the mobility of polymeric segments becomes lower which hamper, in turn, the rotations around simple bonds, so that the flexibility of macromolecules becomes reduced. Under those conditions, the parameter B is determined by the formula

$$B = \frac{\Delta\mu S_c T_0}{k B_1}, \quad (3)$$

where $\Delta\mu$ is an energy barrier, at which the macromolecule changes its conformation; S_c is the minimal

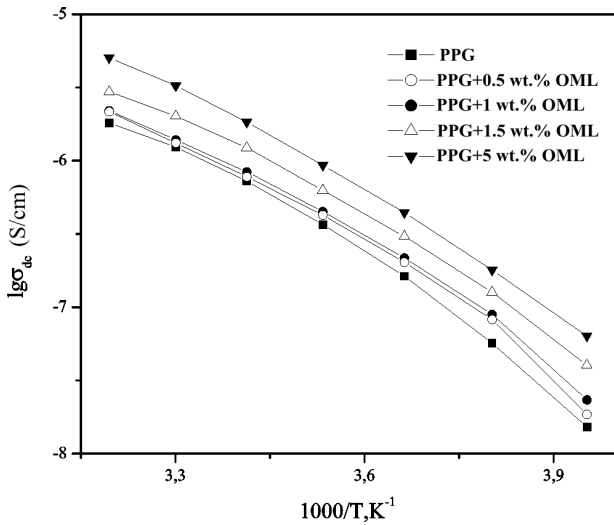


Fig. 2. Temperature dependences of the dc conductivity for nanocomposites on the basis of PPG and OML

configurational entropy needed for disordering; and B_1 is a constant. In this model, the parameter B is the imaginary activation energy of the thermal motion of macromolecular segments [14].

There is another macroscopic model, the authors of which tried to combine the activation character of the charge transfer and the motion of macromolecular segments [15]. To describe the temperature dependence of the conductivity in this model, the Miyamoto–Shibayama (MS) equation is used,

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{\gamma\nu^*}{\alpha\nu_M(T - T_0)} - \frac{\Delta E}{RT}\right), \quad (4)$$

where σ_0 is a constant, ΔE is an energy barrier for the charge transfer, and R is the universal gas constant. If ΔE is very small, it can be neglected, and Eq. (4) transforms into the classical VTF equation. For the treatment of experimental data in the framework of the MS model to be convenient, Eq. (4) can be simplified and written down in the form

$$\ln \sigma_{dc} + \frac{B}{T - T_0} = \ln \sigma_0 + \frac{\Delta E}{RT}. \quad (5)$$

In Fig. 2, the dependences of the dc conductivity on the temperature for PPG + OML-based nanocomposites are depicted. One can see that the nanocomposite conductivity grows with the filler content. This increase, in our opinion, can be explained by the growth of the number of charge carriers owing to Na^+ cations, which OMP is enriched with [16, 17]. The results of the approximation of experimental data by Eq. (1) are quoted in Table.

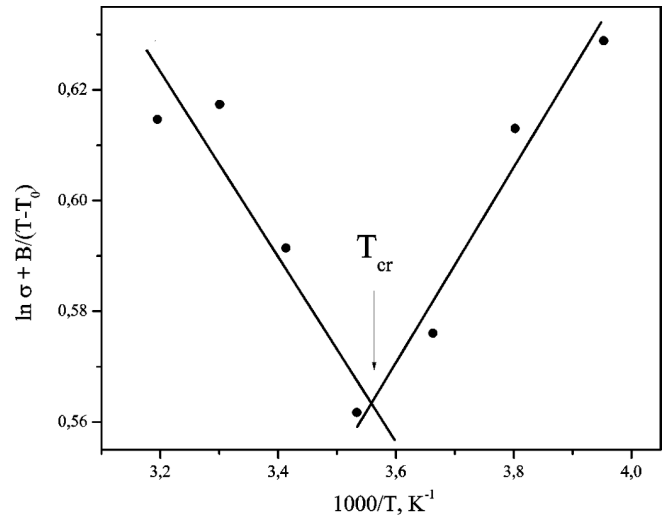


Fig. 3. Temperature dependence of the dc conductivity for PPG + 1.5 wt.% OML in the coordinates of Eq. (5)

To separate the contributions given by the activation and non-activation mechanisms to the charge transfer, the curves from Fig. 2 were replotted in the coordinates of the MS equation. For example, the result of the simulation for a nanocomposite on the basis of PPG + 1.5 wt.% OML is shown in Fig. 3. It is evident that the mechanism of charge transfer changes at a certain temperature T_{cr} . At $T < T_{cr}$, the free-volume mechanism dominates, whereas, at $T > T_{cr}$, the activation one. In Table, the T_{cr} -values and the parameters of the VTF equation for nanocomposites on the basis of PPG and OML are presented. From the table, one can see that the T_{cr} -value is highly dependent on the filler content. At first, it grows with increase in the OML concentration in the system, and then falls down, when the filler content exceeds 1 wt.%.

To estimate the parameters of fragility, D , and free volume, f_g , for pure and filled PPG, we used an approach proposed in work [18]. Using the expressions $D = B/T_0$ and $f_g = (T_g - T_0)/B$ (here, T_g is the vitrification temperature), we calculated D and f_g . According to the classification proposed in [19], this system should

Calculation parameters for the dependences $\sigma(T)$ approximated by the VTF equation and D -, f_g -, and T_{cr} -values for PPG-based systems

PPG	B , K	T_0 , K	T_{cr} , K	D	f_g , %
–	633	189	263	3.3	1.5
0.5 % CNTs	757	180	293	4.2	2.3
1 % CNTs	763	180	297	4.2	2.4
1.5 % CNTs	705	180	283	3.9	2.7
5 % CNTs	1162	152	263	7.6	4.0

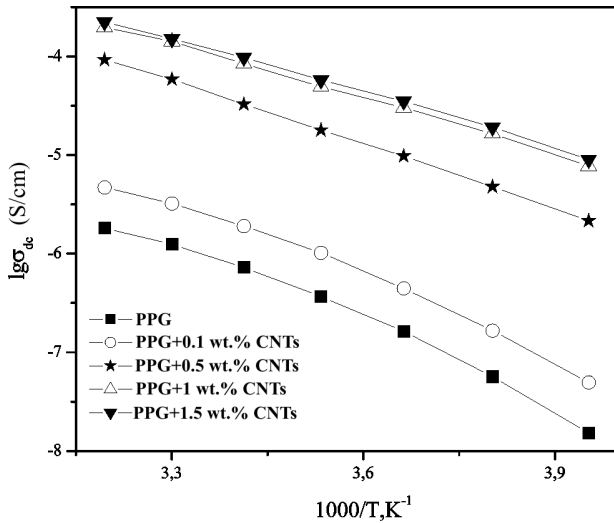


Fig. 4. Temperature dependences of the dc conductivity for nanocomposites on the basis of PPG and CNTs

be classified to “fragile”, which testifies to a considerable influence of the free volume on the charge transport processes in the system. By analyzing the behavior of the parameter f_g (see Table), a conclusion can be drawn about the growth of the free volume fraction with the filler content in the nanocomposite.

In Fig. 4, the temperature dependences of the dc conductivity in nanocomposites on the basis of PPG and CNTs are plotted in the Arrhenius coordinates. The figure demonstrates that the conductivity has an abrupt jump at a CNT content of 0.5 wt.%, which is connected with the emergence of a CNT percolation cluster. To elucidate the contribution of the electronic conductivity of CNTs to the total conductivity of the system, we used the curves in Fig. 3 to calculate the conductivity in unfilled PPG. The results of the subtraction are shown in Fig. 5. From Fig. 5, one can see that, at the introduction of 0.1 wt.% CNTs (below the percolation threshold), the conductivity of the system grows by approximately a half order of magnitude. When the CNT content reaches 0.5 wt.%, the conductivity increases stepwise by almost two orders of magnitude, owing to the emergence of an infinite percolation CNT cluster. Hence, at the introduction of CNTs above the percolation threshold, the conductivity grows at the expense of the electronic component, which is evidenced by the curves in Fig. 5, where the conductivity falls down as the temperature grows.

In Fig. 6, the dependences of the real part of the impedance on its imaginary part are shown for PPG + CNTs systems. The impedance spectra for the given specimens on the basis of PPG consist of a squeezed

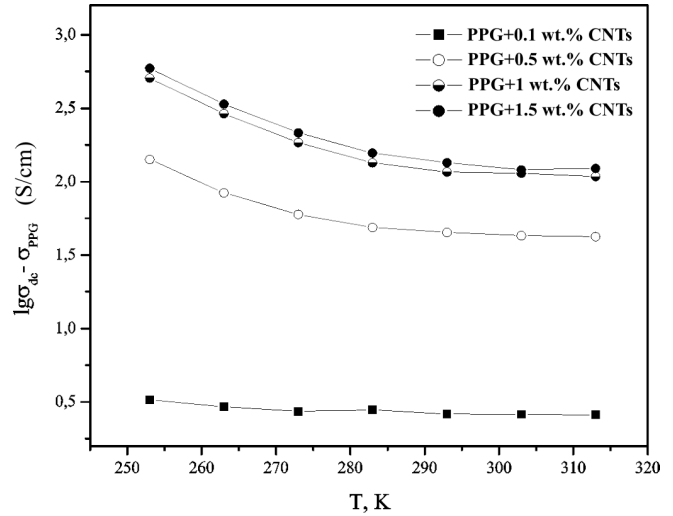


Fig. 5. Results of the subtraction of the unfilled PPG conductivity

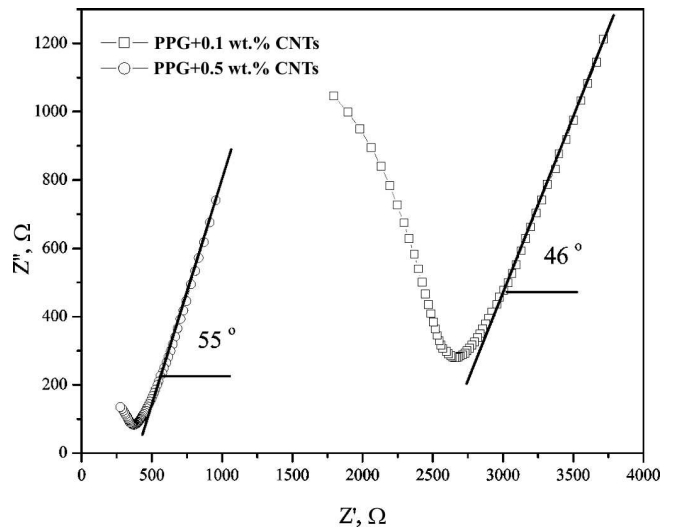


Fig. 6. Dependences Z' versus Z'' for PPG-based nanocomposites at a temperature of 10 °C

arch and an inclined straight line. According to the theory proposed in work [20], the slope of the linear section in the spectrum gives information concerning the charge transfer process in the system. If the slope of the straight line is 45°, there is only one mechanism of charge transfer in the system, e.g., the diffusion. But if the slope differs from 45°, it is possible to talk about the appearance of an additional transfer mechanism.

The slopes of linear sections in the impedance spectra for nanocomposites exhibited in Fig. 6 amount to 46° at a CNT content of 0.1 wt.% and 55° for the specimen containing 0.5 wt.% CNTs. Since the slope angle of 46° is approximately equal to the theoretical angle value

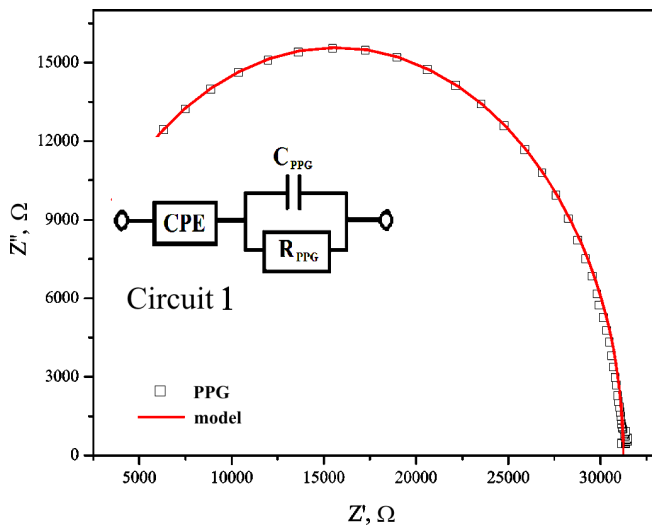


Fig. 7. Impedance spectrum and the corresponding equivalent circuit for unfilled PPG

(45°), we may suppose that there is only one mechanism of charge transfer in the system PPG + CNTs below the CNT percolation threshold; it is the proton transfer, which is provided by the mobility of segments in polyether chains. At the insertion of 0.5 wt.% CNTs (above the percolation threshold), the slope angle becomes different from the theoretical one, which testifies to the emergence of a second mechanism of conductivity, namely, the electron motion through the available CNT cluster [21, 22]. Such a behavior is characteristic of the specimens with CNT contents of 1 and 1.5 wt.%.

The further analysis of the data obtained was carried out by simulating the impedance spectra using the equivalent circuit method and applying the EIS Spectrum Analyser software. This allowed us to quickly and simply attain the complete understanding of charge transfer processes in the system. The impedance of a polymeric material is often modeled as a resistor and a capacitor connected in parallel. To simulate the impedance spectrum of unfilled PPG, we used the equivalent circuit shown in Fig. 7. This circuit demonstrated the complete correspondence to experimental results (Fig. 7). Here, R_{PPG} and C_{PPG} are the total bulk resistance and the geometrical capacity of the material. The constant phase element (CPE) is a generalized universal means for simulating the impedance in a wide class of electrochemical systems. This element can reflect both the exponential distribution of parameters in the given electrochemical reaction, which is connected with the overcoming of an energy barrier at the charge and mass transfer, and the impedance behavior associated with the fractal structure

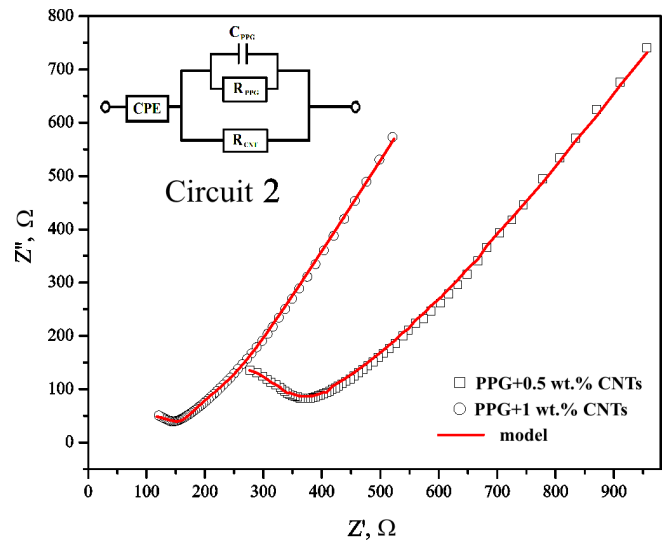


Fig. 8. Impedance spectra and the corresponding equivalent circuit for PPG-based nanocomposites at a temperature of 10 °C

of the surface of an examined specimen. In our model, the CPE is used to compensate inhomogeneities in the system. The impedance of CPE is determined by the following empirical formula:

$$Z_{CPE} = A(j\omega)^{-n}, \tag{6}$$

where A is a proportionality factor, and n is the power exponent, which characterizes the phase deviation.

Hence, as is seen from Fig. 7, the simulation of the impedance of unfilled PPG using equivalent circuit 1 gives rise to the full coincidence between the experimental data and the theoretical results. This testifies to a single type of conductivity in the system; now, it is the proton transfer. However, while attempting to describe the impedance spectra of PPG-based nanocomposites in the framework of equivalent circuit 1 at a CNT content of 0.5 wt.% and higher, the model did not show a correspondence to experimental results. This can be explained by the formation of a CNT percolation cluster and the emergence of another conductivity type, the electronic one. Taking this fact into account, the impedance spectra for nanocomposites were simulated using equivalent circuit 2, into which one more element, R_{CNT} (the resistance of carbon nanotubes), was included [22]. As is seen from Fig. 8, the simulation of the impedance spectra for systems with the CNT content above the percolation threshold using equivalent circuit 2 resulted in the full correspondence to the experimental data. This fact confirms once more the conclusion that there are two types of conductivity, the

ionic and electronic ones, in the PPG + CNTs system.

4. Conclusions

Our researches showed that the application of nanocomposites with the shape anisotropy (OML, CNTs) substantially affects the charge transport processes in polymeric nanocomposites already at extremely low (of about 0.5 wt.%) filler concentrations. The use of the Miyamoto–Shibayama equation allowed us to separate the contributions given by the activation and non-activation mechanisms of charge transfer to the conductivity in the systems filled with laponite. A critical temperature T_{cr} , at which the conductivity mechanism changes, was determined. The T_{cr} -value was found to be highly dependent on the filler content. We also established that PPG + CNTs systems reveal a percolation behavior. The percolation threshold for the given systems falls within the limits of 0.1–0.5 wt.% CNTs. Taking advantage of the equivalent circuit method and the Macdonald theory, we found that two types of conductivity, the ionic and electronic ones, take place in nanocomposites which include carbon nanotubes.

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ВПЛИВ АНІЗОМЕТРИЧНИХ НАПОВНЮВАЧІВ НА ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ НАНОКОМПОЗИТИВ НА ОСНОВІ ПОЛІПРОПІЛЕНГЛІКОЛЮ

Е.А. Лисенков, В.В. Клепко

Резюме

Використовуючи метод імпедансної спектроскопії, проведено дослідження електричних властивостей наноконкомпозитів на основі поліпропіленгліколю та анізотричних нанонаповнювачів. Використання рівняння Міямото–Шибаями дало змогу розділити внески активаційного та неактиваційного механізмів перенесення зарядів у системах, наповнених лапонітом. Визначено критичну температуру, при якій відбувається зміна механізмів. За допомогою методу еквівалентних схем та теорії Макдоналда було встановлено, що в наноконкомпозитах, які містять карбонатотрубки, наявні два типи провідності – іонна та електронна.