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Charge transfer in thin layers of polymer nanocomposites based on aromatic thermoplastic polyimide and cerium dioxide

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Abstract. The results of the study of the electric charge transfer processes in R-OOD polyimide films and in nanocomposite based on it with cerium dioxide are presented. Using the existing model of charge barrier hopping (CBH), the values of the charge transfer parameters, such as the carrier concentration N, free path length R_ω, and potential barrier height W_M are calculated. The activation energy of conductivity processes is determined for all samples. The experimental results made it possible to draw following conclusions about the effect of the filler on the polymer matrix:the power-law nature of the frequency dependence of the specific conductivity σ'(ω) and the decrease in the exponent s with an increase in temperature in a wide range of frequencies and temperatures indicate the existence of a hopping mechanism of conductivity in the R OOD + CeO_2 composite;

charge transfer is a thermally activated process with an activation energy of $E = 0.077$ eV for R-OOD and $E = 0.070$ eV for R-OOD + CeO_2;

the introduction of 3% CeO_2 filler into the R-OOD matrix leads to an increase in the specific conductivity in the low-frequency region and a change in the nature of the hopping mechanism of conduction.

Keywords: electric charge transfer, polyimide, cerium dioxide, charge barrier hopping

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Перенос заряда в тонких слоях полимерных нанокомпозитов на основе ароматического термопластичного полиимида и диоксида церия

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Аннотация. Представлены результаты исследования процессов переноса электрического заряда в полиимидных пленках Р-ООД и в нанокомпозите на его основе с диоксидом церия. С использованием существующей модели прыжков через потенциальный барьер рассчитаны значения параметров переноса заряда, такие как концентрация носителей заряда, длина свободного пробега и высота потенциального барьера. Для всех образцов определена энергия активации процессов проводимости. Результаты экспериментов позволили сделать некоторые выводы о влиянии наполнителя на полимерную матрицу.

Ключевые слова: перенос электрического заряда, полиимид, диоксид церия, прыжковый перенос заряда

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Introduction

Polymer composite materials are widely used in almost all areas of human life. Particular attention is paid to the study of polymer composite materials based on polyimides (PI), as they are characterized by their exceptional mechanical, dielectric, and thermal properties. The possibilities of using these materials are extensive — from industry to microelectronics, medicine, etc. [1–5]. Nevertheless, the issue of using one or another PI-based nanocomposite requires separate studies and detailed analysis.

Various fillers, including nanofibers of metal oxides, which can improve the mechanical and electrical properties of compositions, are used for modifying PI [6–9]. Thus, in composites based on PI and cerium dioxide nanoparticles a number of important results have been obtained concerning thermal stability and mechanical properties [9]. However, no attention has been paid in these studies to the study of charge transfer processes in these materials. That is why the purpose of this work was to establish the features of charge transfer processes in polymer composites based on aromatic polyimide R-OOD with cerium dioxide as a filler by the dielectric spectroscopy method.

Materials and Methods

The objects of study in present work were the initial R-OOD and the nanocomposite R-OOD + 3% CeO_2. In these PIs the anhydride part of the macromolecule was 1,3 bis (3',4 dicarboxyphenoxy)benzene dianhydride, and 4,4'-bis-(4"-aminophenoxy)diphenyl oxide (R-OOD) was used as the diamine. Polyimide films were obtained in Institute of Macromolecular Compounds of the Russian Academy of Sciences by a standard two-stage method [1, 10]. Cerium dioxide CeO_2 (3%) was used as a nanofiller. The films of 25–50 µm thick were pressed between brass electrodes and additionally heated to 250 K.

To study the surface structure and determine the elemental composition of the samples, a Carl Zeiss EVO 40 scanning electron microscope was used. This measuring system is designed to obtain images of objects in “forward” and backscattering electrons with a maximum resolution of several nanometers.

The dielectric response of the samples was obtained using a Concept-81 broadband dielectric spectrometer (NOVOCONTROL Technologies GmbH&Co) with an ALPHA-ANB high-resolution automatic frequency analyzer (core shared research facilities “Modern physical and chemical methods for the formation and study of materials for the needs of industry, science, and education”/Herzen University). To study the transfer processes in R-OOD and R-OOD + CeO_2, an alternating electric field with a frequency $f = 10^{-1}–10^{7}$ Hz was applied to the samples in the temperature range $T = 173–253$ K.

Results and Discussion

The frequency dependences of the specific conductivity for R-OOD and R-OOD + CeO_2 at various temperatures are shown in Figures 1 and 2, respectively.

As follows from the figure, the dispersion σ′ complies with the law:

$$\sigma'(\omega) = A\omega^{S} \tag{1}$$

here ω is the angular frequency, A is a frequency-independent constant, and *s* is the exponent.

This type of dependence is characteristic for many disordered systems, such as glassy and amorphous semiconductors, polymer systems and composite materials based on them [11]. The values of the power dependence parameter were determined by approximating the experimental data using a linear function (the relative error did not exceed 3% over the entire temperature range).

The temperature dependence of the parameter s is shown in Figure 3 for R-OOD and R-OOD + CeO_2. Qualitative differences in the temperature dependences of the parameter s indicate a change in the conductivity mechanism in samples with 3% CeO_2 nanoparticles.

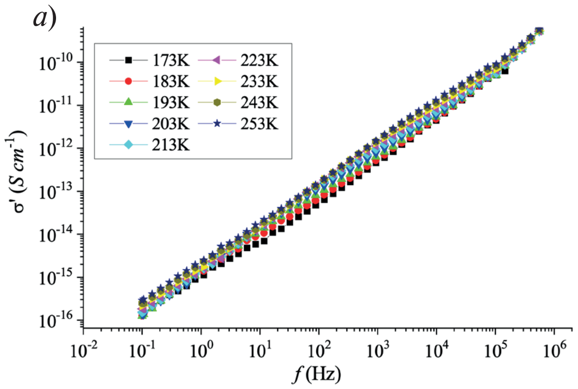

Fig. 1. Frequency dependence of specific conductivity σ′ at different temperatures for R-OOD

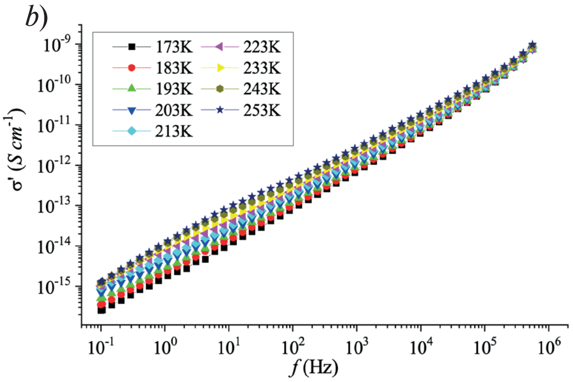

Fig. 2. Frequency dependence of specific conductivity σ′ at different temperatures for R-OOD + CeO_2

The temperature dependence of the parameter s is shown in Figure 3 for R-OOD and R-OOD + CeO_2. Qualitative differences in the temperature dependences of the parameter s indicate a change in the conductivity mechanism in samples with 3% CeO_2 nanoparticles.

The existence of an exponential dependence of specific conductivity σ' on temperature (Fig. 4 and 5) allows us to conclude that charge transfer in the systems under study is a thermally activated process obeying the Arrhenius law [12]. The activation energy E was calculated from the slope of the curves $\ln\sigma' = f(10^3/T)$. The *E* values for R-OOD and R-OOD + CeO_2 are 0.077 and 0.070 eV, respectively (the relative calculation error did not exceed 3%). The introduction of 3% CeO_2 into the R-OOD polyimide matrix leads to an increase in the specific conductivity in the low-frequency region. This can be associated with structural changes in the polymer matrix (Fig. 6).

For R-OOD + CeO_2, the power dependence of conductivity on frequency (Fig. 6, curve 1), as well as the decrease in the functional parameter s with temperature from 0.94 to 0.79 (Fig. 3, curve 2), are apparently associated with the manifestation of the hopping mechanism of conductivity. There are several models for hopping charge transfer; the linear drop in the temperature dependence of s can be explained in terms of the CBH model (correlated barrier hopping model) [13]. It is assumed that the charge transfer is carried out by electrons jumping between energy states, overcoming the potential barrier *W* between two localized states (equilibrium centers). In this case, the height of the barrier between two localization centers is determined by the Coulomb interaction between neighboring defect (impurity) states, which can be charged formations in the structure that form a dipole.

According to the authors of [14], the expression for alternating current is as follows:

$$\sigma'(\omega) = \frac{\pi^3 N^2 \varepsilon\varepsilon_0 \omega R_\omega^6}{24}, \tag{2}$$

here *N* is the density of the pairs of states, R_ω is jump length, ω is angular frequency.

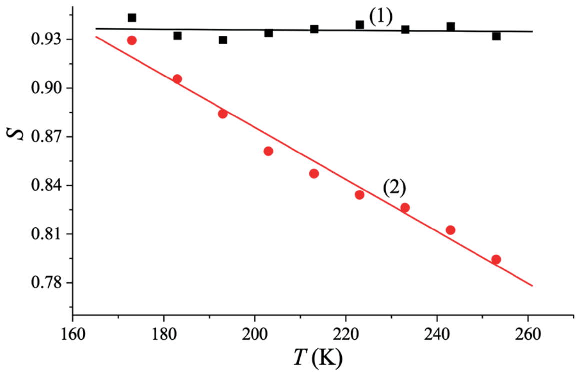

Fig. 3. Temperature dependence of the exponent s from Equation (3) for samples R-OOD — (1), and R-OOD + CeO_2 — (2)

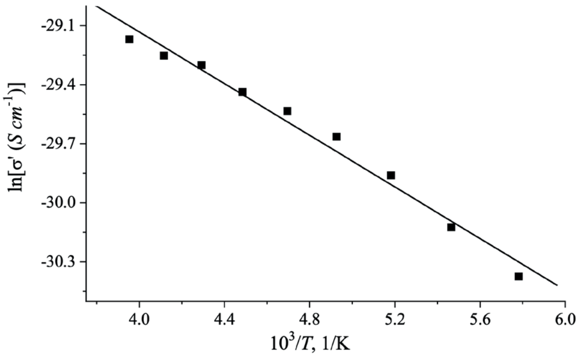

Fig. 4. Temperature dependence of specific conductivity σ' for R-OOD

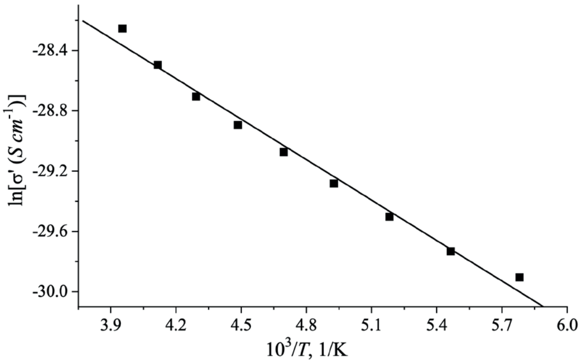

Fig. 5. Temperature dependence of specific conductivity σ' for R-OOD + CeO_2

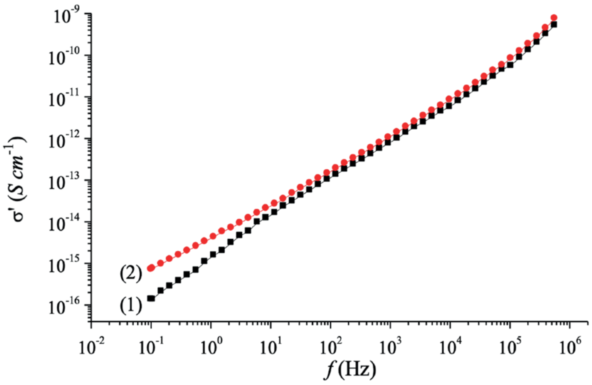

Fig. 6. Frequency dependence of specific conductivity at $T = 203$ K. (1) — R-OOD ($s = 0.94$); (2) — R-OOD + CeO_2 ($s = 0.86$)

The relationship between R_ω and the height of the potential barrier W_M can be expressed by the equation:

$$R_\omega = \frac{e^2}{\pi \varepsilon \varepsilon_0} \left[W_M - kT \ln\left(\frac{1}{\omega \tau_0}\right) \right]^{-1}, \tag{3}$$

here τ_0 is the characteristic relaxation time (the reciprocal of the phonon frequency ν_{ph}).

Theoretically, it is shown that the exponent s is related to the barrier height W_M by the expression:

$$s = 1 - \frac{6kT}{W_M}. \tag{4}$$

Equations (2–4) can be used to calculate the microparameters N, R_ω, and W_M for the systems under study over the entire temperature range (Table 1).

The observed patterns of charge transfer processes in the R-OOD + CeO_2 nanocomposite, the change in the nature of the hopping mechanism of the charge transfer, and the increase in conductivity are associated with the introduction of a filler — cerium dioxide nanoparticles.

X-ray study (EDX — energy-dispersive X-ray) of PI + CeO_2 nanocomposites showed that if in the initial R-OOD there is a uniform distribution of particles in the sample, then in the R-OOD + CeO_2 nanocomposite the formation of CeO_2 aggregates of various sizes is observed [9]. The appearance of intrinsic structures of cerium dioxide in the polymer matrix can lead to the formation of continuous conducting channels, which in turn leads to an increase in conductivity. A similar situation was observed in a nanocomposite based on polyphenylene oxide with fullerene [15].

Table 1

Values of microparameters of R-OOD polyimide calculated within the framework of the CBH model

T (K)	s	N (m^{-3})	R_ω (nm)	W_M (eV)
173	0.94	$2.10.10^{23}$	2.20	1.27
183	0.91	$7.51.10^{22}$	3.19	1.00
193	0.88	$3.48.10^{22}$	4.28	0.86
203	0.86	$1.54.10^{22}$	5.84	0.75
213	0.85	$1.02.10^{22}$	6.92	0.72
223	0.83	$6.63.10^{21}$	8.23	0.70
233	0.82	$5.51.10^{21}$	9.04	0.69
243	0.81	$3.18.10^{21}$	11.12	0.67
253	0.79	$1.23.10^{21}$	16.08	0.64
Error	≤ 3.0%	≤ 5.0%	≤ 5.0%	≤ 5.0%

Conclusion

In this work the dielectric method is used for the first time to study the features of charge transfer processes in R-OOD polyimides films and a nanocomposite based on it with cerium dioxide as a filler. Conductivity parameters were calculated within the framework of the CBH conductivity model. The main conclusions of the work are as follows:

1. The power-law nature of the frequency dependence of the specific conductivity $\sigma'(\omega)$ and the decrease in the exponent s with an increase in temperature in a wide range of frequencies and temperatures indicate the existence of a hopping mechanism of conductivity in the R-OOD + CeO_2 composite.
2. Charge transfer is a thermally activated process with an activation energy of $E = 0.077$ eV for R-OOD and $E = 0.070$ eV for R-OOD + CeO_2.
3. The introduction of 3% CeO_2 filler into the R-OOD matrix leads to an increase in the specific conductivity in the low-frequency region and a change in the nature of the hopping mechanism of conduction.

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