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Characteristic Features of the Charge Transfer Processes in the Nanocomposites Based on Polyphenylene Oxide with Fullerene and Endofullerene

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Abstract—The results of the study of the electric charge transfer processes in polymer nanocomposites based on polyphenylene oxide with fullerene C_{60} (1, 8%) and endometallofullerene Fe@C_{60} (1%) as the nanofillers are presented. 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 using the existing theoretical models. The conductivity type was determined for all the samples by the analysis of the temperature dependences of the exponent s.

Keywords: charge transfer, hopping conduction mechanism, quantum mechanical tunneling, polymer nanocomposites, fullerene, endometallofullerene

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1. INTRODUCTION

Polymers are ideal matrices for creating new materials with set properties, in particular, for obtaining versatile membranes. Membranes are used in the processes of concentration and fractionation of mixtures, purification of products from related impurities, in the regeneration of valuable components, for obtaining desalted and purified water, and in solving environmental problems. Recently, polyphenylene oxide (PPO) membranes as well as composites based on it have proven themselves well [1–3]. Modifications of PPO with various types of fillers lead to substantial changes in its dielectric, structural, and diffusion properties. Allotropic forms of carbon, one of which is fullerene (C_{60}), are widely implemented to improve the properties of membranes [4].

Nanocomposites with donor–acceptor complexes are formed upon modifying PPO with fullerene C_{60}. A study of solutions of this complex by rheological and hydrodynamic methods showed [5] that the bond of PPO with C_{60} is quite stable because the complex does not break into components even upon dilution, although there is a slight decrease in the intrinsic viscosity and asymmetry of the shape of the PPO segments. It has been shown by mass spectrometric thermal analysis and differential calorimetry that adding fullerene to PPO increases its thermal stability [6]. The presence of molecular complexes in the PPO/C_{60} films containing up to 2 wt % C_{60} has been found upon studying the photoluminescence spectra. Upon increasing the concentration, a significant part of C_{60} molecules is in not bonded to PPO molecules starting from 4% [7].

So-called endohedral fullerenes containing metal and nonmetal atoms in the inner cavity of the fullerene cage are of interest along with the well-studied fullerenes C_{60}. Such inclusions change the electrophysical properties of the fullerene molecule and, hence, the polymer composite.

The charge transfer processes in polymer nanocomposites based on PPO with fullerene C_{60} and endometallofullerene Fe@C_{60} are studied in this work. The aim of this work is to reveal the effect of C_{60} and Fe@C_{60} fillers on the electrophysical properties of the nanocomposite.

2. EXPERIMENTAL

The polymer matrix was PPO with a molecular weight (MW) = 178000 g/mol and a density of 1.06 g/cm^3. Fullerene C_{60} and endometallofullerene Fe@C_{60} containing over 99.5 wt % C_{60} (OOO Fullerenovye Tekhnologii, Russia) were used as the nanoadditive. The PPO/C_{60} and PPO/Fe@C_{60} composites were prepared by mixing solutions of PPO in chloroform and fullerene/endofullerene in toluene. The films were obtained on the surface of cellophane in a round mold that was filled with a calculated amount of

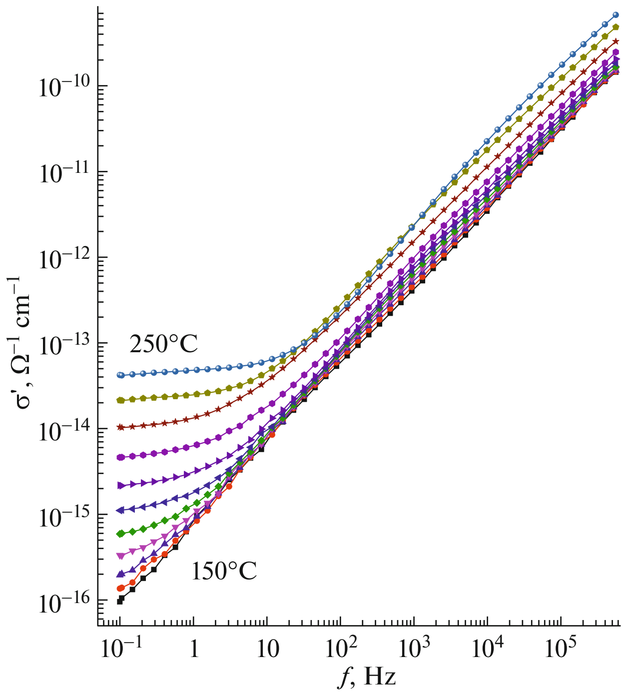

Fig. 1. Dependence of the real part of complex conductivity on the alternating field frequency at temperatures of 150 to 250°C for PPO/$C_{60(1\%)}$. The temperature step is 10°C.

a 2% solution of the polymer. The thickness of the films was 30–100 μm. This work presents the results of the study of the samples with the following compositions: PPO/$C_{60(1\%)}$, PPO/$C_{60(8\%)}$, PPO/Fe@$C_{60(1\%)}$, and pure PPO. The choice of the samples was determined by the particular fact that, in the case of PPO/$C_{60(1\%)}$ and PPO/Fe@$C_{60(1\%)}$, the filler is in the molecularly dispersed form in the polymer matrix when there is a chemical bond between molecules of the polymer and the filler [8, 9]. Further increasing the filler content (already at 4%) leads to the formation of fullerene clusters, the concentration of which will a priori be higher in the PPO/$C_{60(8\%)}$ film. Therefore, it was interesting to compare the electrophysical properties of the nanocomposites with qualitatively different structures.

The electrical conductivity spectra were recorded on a Concept-81 dielectric spectrometer (Novocontrol Technologies GmbH). To obtain experimental data, the film samples were placed between brass electrodes (the diameter of the upper electrode was 20 mm). Temperature–frequency dependences of the real part of complex conductivity σ' were obtained for the samples of the PPO, PPO/$C_{60(1\%)}$, PPO/$C_{60(8\%)}$, and PPO/Fe@$C_{60(1\%)}$ systems in a range of frequencies of 10^{-1}–10^6 Hz and a range of temperatures of –100–+250°C. The accuracy of the control of the temperature on the sample was ±0.5°C. The voltage applied to the sample was $U = 1.0$ V.

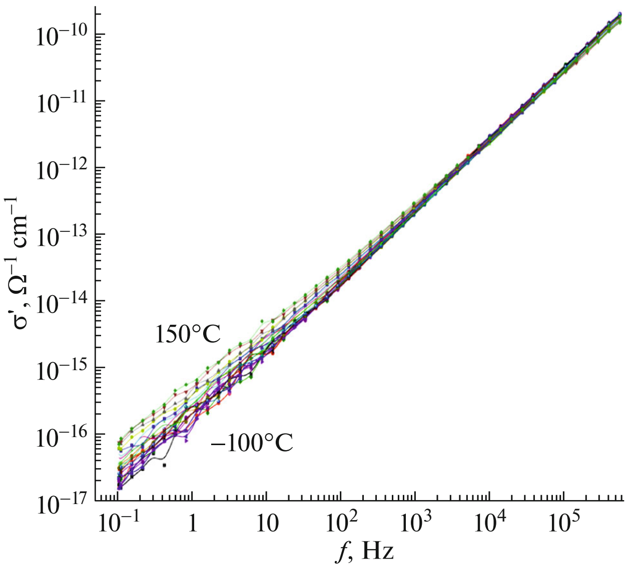

Fig. 2. Dependence of the real part of complex conductivity on the alternating field frequency at temperatures of –100 to 150°C for PPO/$C_{60(1\%)}$. The temperature step is 10°C.

3. RESULTS AND DISCUSSION

The frequency dependences of the real part of complex conductivity σ'(*f*) on the double logarithmic scale for PPO/$C_{60(1\%)}$ in a temperature range from 150 to 250°C are presented in Fig. 1.

The σ'(*f*) dependences show a linear increase in the conductivity with increasing frequency in a temperature range of –100 to 150°C (Fig. 2). Then a kink (at a frequency f_0) appears at higher temperatures upon transition to the frequency-independent region of σ'(*f*) at low frequencies. The kink frequency f_0 in the dependence σ'(*f*) increases with the increase in temperature. The dependences σ'(*f*) are qualitatively similar for the samples with other compositions.

In many amorphous semiconductors and dielectrics, the conductivity in an electric field has the form [10]

$$\sigma'(\omega) = A\omega^s. \quad (1)$$

The linear increase in σ' with the increase in frequency (according to the power law) indicates a hopping conduction mechanism. The transition from the frequency-independent region to the frequency-dependent region means the onset of conductivity relaxation [11].

In the region of low frequencies ($f < 10$ Hz), the maximum number of polarization processes is activated in the material; here, the spatial motion of the charged particles in an almost constant (quasi-stationary) electric field is limited by potential barriers and structural defects which prevent the transfer of electric charges from electrode to electrode. The charged particles do not manage to orientate themselves with the increasing frequency of the electric field and, continuously following the change in the electric field, contribute to the conductivity. Their contribution to the polarization is simultaneously "switched off", which manifests itself in a decrease (dispersion) of the dielectric permeability [8, 9]. This phenomenon is called conductivity relaxation.

The continuous increase in the conductivity in a very wide range of frequencies (from 10^1 Hz) is explained by the difference in the values of potential barriers to be overpassed by charged particles for recombination due to the absence of any order in the polymer material. It should be expected that the dependence $\sigma'(f)$ will again reach a "plateau" at higher frequencies. This will mean that all the charge carriers do not manage to reach the localized states and, hence, will participate in charge transfer—the conductivity in the material will reach a maximum.

Apparently, the conductivity in the materials under study also depends on temperature. However, the effect of temperature is more obvious in the low-frequency range, while the values of σ' are close for different temperatures and are $\approx 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$ in the region of high frequencies, evidencing that the materials under study fall on the boundary between semiconductors with the conductivity $\sigma = 10^{4}$–$10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$ and dielectrics with $\sigma = 10^{-10}$–$10^{-22}\ \Omega^{-1}\ \text{cm}^{-1}$.

The transition from the frequency-independent part of the spectrum to the frequency-dependent part occurs at a frequency f_0 and evidences the onset of conductivity relaxation. The value of f_0 shifts to the region of high frequencies with increasing temperature, which is associated with a decrease in the potential barrier between the localized states of the charge carriers. As is seen from Fig. 1, the conductivity relaxation at 250°C already begins at a frequency $f_0 = 3 \times 10^1$ Hz. With decreasing temperature, the above transition already disappears at 150°C, and only the frequency-dependent region of the spectrum remains in the graph (Fig. 2).

The dynamics of the change in the value of the exponent s (formula (1)) on temperature is an important factor when determining the type of conductivity in a material. The exponent s increases with increasing temperature in the case of quantum mechanical tunneling (QMT) [12]; $s = 1$ within the model of classical mechanism of hopping over the potential barrier (HOB) [13]; and s decreases with increasing temperature in the model of correlated barrier hopping (CBH) [14]. Two models of charge transfer are most often observed in polymer materials, namely quantum mechanical tunneling and correlated hopping over the potential barrier.

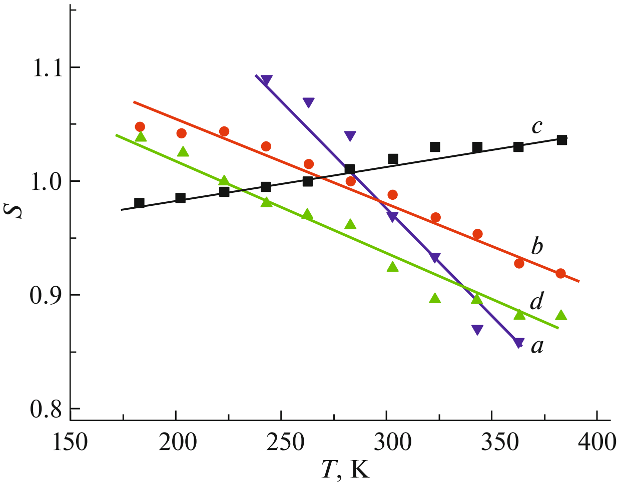

Fig. 3. Dependence of the exponent s on temperature for the samples of (*a*) pure PPO, (*b*) PPO/$C_{60(1\%)}$, (*c*) PPO/Fe@$C_{60(1\%)}$, and (*d*) PPO/$C_{60(8\%)}$.

According to the correlated barrier hopping (CBH) model, electrons hop in an electric field, overpassing the potential barrier:

$$W = W_\text{M} - \frac{ne^2}{\pi\varepsilon\varepsilon_0 r}, \tag{2}$$

where W_M is the maximum potential barrier height, ε is the dielectric permeability of the material, ε_0 is the dielectric permeability of vacuum, r is the distance between two positions of the charge carrier, and n is the number of hopping electrons (n takes the values of 1 and 2 for the cases of polaron and bipolaron processes, respectively).

Within the CBH model, the expression for alternating current conduction is as follows:

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

Here, N is the density of the pairs of states, between which charge carriers hop.

The relationship between the hop distance R_ω and potential barrier height is expressed by the correlation

$$R_\omega = \frac{e^2}{\pi\varepsilon\varepsilon_0}\left[W_\text{M} - kT\ln\left(\frac{1}{\omega\tau_0}\right)\right]^{-1}. \tag{4}$$

On the other hand, the exponent s is tied to the potential barrier height W_M by the expression

$$s = 1 - \frac{6kT}{[W_\text{M} - kT/(\omega\tau_0)]}. \tag{5}$$

Formula (5) can be simplified on the first approximation:

$$s = 1 - \frac{6kT}{W_\text{M}}. \tag{6}$$

Table 1. Value of the charge transfer parameters in pure PPO

t, °C	f, Hz	s	N, $m^{-3} \times 10^{22}$	R_ω, $m \times 10^{-10}$	W_M, eV
100	1.1×10^6	0.88	10.1	28.4	1.5
	9838.8		6.9	32.6	
	1.5		4.7	44.8	
50	1.1×10^6	0.90	10.0	28.2	1.6
	9838.8		5.9	31.5	
	1.5		5.9	40.6	
30	1.1×10^6	0.96	213.1	10.2	3.7
	9838.8		133.7	10.5	
	1.5		225.2	11.2	

Table 2. Value of the charge transfer parameters in the $PPO/C_{60(1\%)}$ composite

t, °C	f, Hz	s	N, $m^{-3} \times 10^{22}$	R_ω, $m \times 10^{-10}$	W_M, eV
100	1.1×10^6	0.92	44.0	13.8	2.4
	9838.8		41.9	14.9	
	1.5		36.6	17.7	
50	1.1×10^6	0.95	233.1	8.1	3.7
	9838.8		216.2	8.4	
	1.5		200.6	9.2	
30	1.1×10^6	0.99	3537.0	2.1	13.1
	9838.8		12132.1	2.1	
	1.5		13586.6	2.2	

Table 3. Value of the charge transfer parameters in the $PPO/C_{60(8\%)}$ composite

t, °C	f, Hz	s	N, $m^{-3} \times 10^{22}$	R_ω, $m \times 10^{-10}$	W_M, eV
100	1.1×10^6	0.86	3.9	36.4	1.3
	9838.8		1.4	43.7	
	1.5		1.7	69.0	
50	1.1×10^6	0.93	53.2	15.5	2.5
	9838.8		22.6	16.5	
	1.5		38.2	18.9	
30	1.1×10^6	0.97	608.9	6.7	5.2
	9838.8		316.6	6.9	
	1.5		517.3	7.2	

The values of the exponent s were calculated by linear approximation of the experimental curves (Fig. 2) to identify the type of conductivity in the materials under study; the dependences of the exponent s on temperature are presented in Fig. 3.

It is seen from Fig. 3 that the exponent s decreases with increasing temperature for (*a*) pure PPO, (*b*) $PPO/C_{60(1\%)}$, and (*d*) $PPO/C_{60(8\%)}$. A relatively slow increase in the exponent s with increasing temperature is found for PPO with endohedral fullerene.

It can be assumed that the CBH model corresponds to the samples of $PPO/C_{60(1\%)}$, pure PPO, and $PPO/C_{60(8\%)}$.

The values of the parameters N, R_ω, and W_M at different temperatures were calculated for the samples under study from formulae (2)–(6) (see Tables 1–3). It was obtained that the potential barrier height decreased with increasing temperature.

As opposed to pure PPO, $PPO/C_{60(1\%)}$, and $PPO/C_{60(8\%)}$, the film of $PPO/Fe@C_{60(1\%)}$ manifests an increase in the exponent s with increasing temperature, which is observed within the model of quantum mechanical tunneling (QMT). The molecular mechanism of such a behavior requires further investigation.

As it was mentioned earlier, both charge transfer mechanisms are observed in most polymers including PPO; however, one of them is always predominant. It was found in this work that changes were observed in the composite material upon introducing an iron atom into fullerene, as a result of which a change in the leading type of conductivity, i.e., transition from the hopping of charge carriers over the potential barrier to quantum mechanical tunneling, occurs. This may be caused by the pronounced metallic properties of iron. The iron atom encapsulated in a fullerene molecule acts as an electron donor. The metal atoms pass their valence electrons to the outer surface of the fullerene shell, thus changing the total charge of the particles of the filler.

4. CONCLUSIONS

As a result of studying the electric charge transfer processes in the nanocomposites based on PPO with fullerene and endometallofullerene, a transition from the frequency-independent to the frequency-dependent region has been found in the dependences $\sigma'(f)$, during which the process of conductivity relaxation begins. The conductivity in the samples of PPO and PPO with fullerene has a predominantly hopping character, i.e., it is in agreement with the model of correlated barrier hopping (CBH). The type of conductivity changes in the case of introduction of Fe into C_{60}; charge transfer due to quantum mechanical tunneling begins predominating in the material. The values of the charge transfer parameters have been calculated for the samples of $PPO/C_{60(1\%)}$, pure PPO, and

$PPO/C_{60(8\%)}$. It has been found that the height of the potential barrier overpassed by the charged particles that follow the electric field decreases with increasing temperature. The highest values of the potential barrier height W_M correspond to the composition $PPO/C_{60(1\%)}$ when the filler is in the polymer matrix in the molecularly dispersed form, and a chemical bond is observed between the molecules of the polymer and the filler.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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