

Effect of quasi-stationary electric field on charge transfer in poly(phenylene oxide) based composites

A. A. Kononov^{✉1}, R. A. Castro Arata¹, N. A. Nikonorova²

¹ Herzen State Pedagogical University of Russia, 48 Moika River Emb., Saint Petersburg 191186, Russia

² Institute of Macromolecular Compounds of Russian Academy of Sciences, 31 Bolshoy Avenue, Saint Petersburg 199004, Russia

Authors

Alexey A. Kononov, ORCID: [0000-0002-5553-3782](https://orcid.org/0000-0002-5553-3782)

Rene Alejandro Castro Arata, ORCID: [0000-0002-1902-5801](https://orcid.org/0000-0002-1902-5801)

Natalia N. Nikonorova, ORCID: [0000-0002-7928-9227](https://orcid.org/0000-0002-7928-9227)

For citation: Kononov, A. A., Castro Arata, R. A., Nikonorova, N. A. (2020) Effect of quasi-stationary electric field on charge transfer in poly(phenylene oxide) based composites. *Physics of Complex Systems*, 1 (2), 52–55.
DOI: 10.33910/2687-153X-2020-1-2-52-55

Received 13 January 2020; reviewed 27 February 2020; accepted 27 February 2020.

Copyright: © The Authors (2020). Published by Herzen State Pedagogical University of Russia. Open access under CC BY-NC License 4.0.

Abstract. The article explores the processes of charge transfer in the samples of polymeric composites based on poly(phenylene oxide) with fullerene and endometalfullerene in the electric field of low frequencies ($f = 10^{-1}$ Hz). The article identifies transfer processes connected with intramolecular and intermolecular conductivity. It is found that conductive channels are formed in a polymeric matrix at high concentrations of fullerene, thus, the type of conductivity changes from semiconductor to metallic. The embedding of iron into the fullerene frame molecule leads to the appearance of metallic conductivity of the composite in some temperature range.

Keywords: dielectric relaxation, charge transfer, polymeric composites.

Introduction

In recent years, research has been focusing on the development of polymeric composite materials (PCM) with high dielectric permittivity. These materials have large potential for application in various industrial technologies, namely electronics and automobile manufacturing (Cha, Kim, Hwang et al. 2012). Polyphenylene oxide (PPO) is considered to be one of the most promising polymers in the synthesis of composites. When modified, PPO changes its electrophysical properties significantly. Currently, fullerene (C_{60}) and endohedral carbon clusters, i.e., fullerenes with atoms of metals and nonmetals embedded into their cavity, have attracted considerable interest as polymer modifiers. Our prior research was limited to the analysis of photoluminescence spectra, IR absorption spectra and gas diffusion through films of fullerene-containing polyphenylene oxide (Polotskaya, Penkova, Toikka et al. 2007). The purpose of this research is to determine an effect of quasi-stationary electric field (low frequencies) on the charge transfer in the polyphenyleneoxide based composites with fullerene as a filler.

Experimental methods

The composites were obtained by mixing solutions of PPO in chloroform (concentration 2 wt.%) and fullerene C_{60} or endofullerene $Fe@C_{60}$ in toluene (concentration 0.14 wt.%) in the amounts that provide

the desired content of fillers. Thus obtained, the solution was left for 3–4 days to achieve the interaction between the polymer and the fullerene molecules. Then, the solution of the composite was processed with ultrasound for 40 min. and filtered through the Shot's filter to remove dust impurities. The films were obtained by casting 2 wt.% polymer solutions on a cellophane surface with subsequent solvent evaporation at 313K and drying in vacuum at 313K up to constant weight (Biryulin, Melenevskaya, Mikov et al. 2003).

The surface morphology and composition of the samples was studied by scanning electron microscopy EVO 40. The scan of the surface of PPO/C_{60(4%)} sample is shown in Figure 1.

The measurement of the dielectric spectra was carried out on the spectrometer "Concept 81" (NOVOCONTROL Technologies GmbH) with the automatic ALPHA-ANB high performance frequency analyzer. The samples were films of a thickness of 60–125 μm and of a diameter of 20 mm. Temperature dependences of the real part of the complex conductivity σ' were obtained for samples of PPO/C_{60(8%)}, PPO/C_{60(4%)}, PPO/C_{60(1%)}, and pure PPO in the temperature range between 173 K and 523 K at 10⁻¹ Hz and at applied voltage 1.0 V.

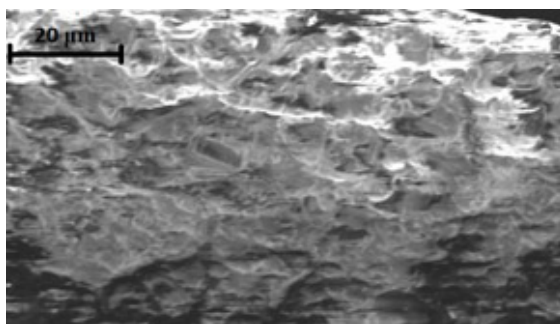


Fig. 1. Scan of a slice of the PPO/C_{60(4%)} sample at a resolution of 20 μm

Results and discussion

Specific conductivity or its reciprocal value—the specific electrical resistance of polymers—is conditioned by the existence of free charges (electrons and ions) that are characterized by mobility. Polymer chains themselves do not contribute to the transfer of electric charges. Free charges that are not chemically bound to the macromolecules are probably due to low molecular weight ionic impurities whose mobility is limited by the high viscosity of the environment. Therefore, the electrical conductivity of polymers is extremely low, and the electrical resistance is very high (Polotskaya, Lebedev, Gofman, Vinogradova 2017).

To estimate the activation energy of conductivity, temperature dependences of natural logarithm of the real part of the complex conductivity σ' at 10⁻¹ Hz for PPO/C_{60(8%)}, PPO/C_{60(1%)}, and pure PPO were plotted and presented in Figures 2, 3, and 4 respectively. These dependences show two temperature ranges which can be approximated by straight lines corresponding to the Arrhenius equation (Jonscher 1996):

$$\sigma' = \sigma'_0 \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where σ'_0 —pre-exponential factor,

E_a —conductivity activation energy.

The values of the activation energy and the pre-exponential factor for the two ranges on the curves of temperature dependence σ' that were measured using the formula (1) are presented in Table for all measured samples. The error in the activation energy values assessment does not exceed 4.5%.

We can assume that low and high temperature ranges corresponding to different activation energy values could be attributed to the existence of intermolecular and intramolecular types of conductivity respectively.

When transferred intramolecularly, the electrons can “jump” from atom to atom, provided these atoms have electron orbitals with equal energy values. If the molecules overlap, the electrons move from

Table. Parameters of electrical conductivity of investigated samples at $f = 10^{-1}$ Hz

Samples	E_{aI} , eV	E_{aII} , eV	σ_{0I} , $\text{Ohm}^{-1}\text{cm}^{-1}$	σ_{0II} , $\text{Ohm}^{-1}\text{cm}^{-1}$
PPO	0.09	0.75	$6.6 \cdot 10^{-15}$	$4.12 \cdot 10^{-6}$
PPO/ _{C₆₀(1%)}	0.08	1.37	$3.1 \cdot 10^{-16}$	$4.88 \cdot 10^{-1}$
PPO/ _{C₆₀(4%)}	0.23	1.19	$7.2 \cdot 10^{-13}$	$1.04 \cdot 10^{-1}$
PPO/ _{C₆₀(8%)}	0.28	1.17	$9.6 \cdot 10^{-12}$	$5.70 \cdot 10^{-2}$

macromolecule to macromolecule. The first conductivity stage with lower activation energy values is specific for the intermolecular charge transfer (range II), while higher activation energy values correspond to intramolecular charge transfer (range I).

Figure 2 shows that for temperatures 333–403 K the specific conductivity for PPO/_{C₆₀(8%)} (the highest concentration of C_{60} in composite) increases when temperature decreases. This picture is typical of metallic conductivity. It can be assumed that at high concentrations of fullerene in the polymer matrix, C_{60} molecules form conductive channels, which changes the type of conductivity from semiconductor to metallic. Figure 1 clearly shows fullerene regions—the black areas are clusters of C_{60} molecules. With a further increase in temperature (above 403 K), the conductivity behavior is dielectric again: with temperature increasing, the electrical conductivity increases too. This may be the result of the destruction of conductive channels by increased temperatures.

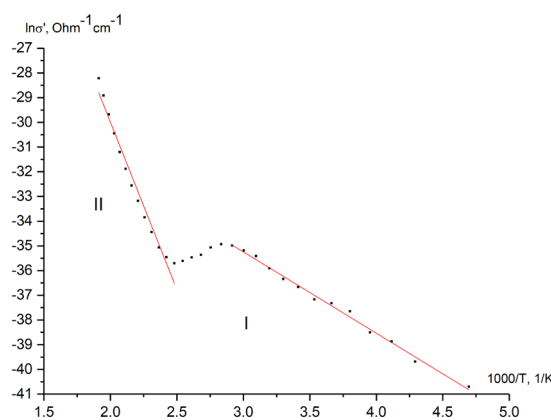


Fig. 2. Electron energy loss spectra for Mg. $E_p = 100$ eV. $\phi = 80^\circ$. Emergent angles α are specified near the curves

Moreover, the region of metallic conductivity is observed in the samples of fullerene PPO/Fe@_{C₆₀(1%)} with embedded iron atoms (Figure 3) at temperatures below 60°C, which is due to clearly displayed metallic properties of iron. The samples which do not contain iron in the fullerene frame, like PPO/_{C₆₀(1%)} (Figure 3) and the pure PPO (Figure 4), are only characterized by the semiconductor type of conductivity in the temperature range $t = 173$ – 523 K. At temperatures above 443 K, the conductivity dependences for the samples with endometallofullerene and fullerene are very similar. At low temperatures the conductivity of samples with embedded iron begins to increase, while the conductivity of iron-free samples continues to decrease. The metallic type of conductivity in PPO/Fe@_{C₆₀} samples is the result of the growing concentration of conduction electrons with the increase of endofullerene content in the polymer matrix. An iron atom encapsulated in a fullerene molecule becomes an electric donor. The metal atoms transfer their valence electrons to the external surface of the fullerene frame, increasing the conductivity of the samples.

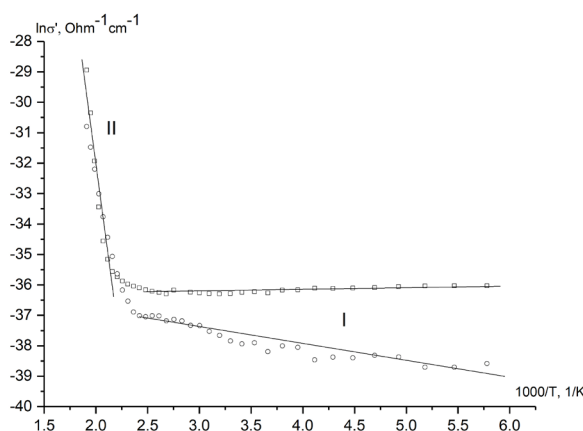


Fig. 3. Temperature dependence of specific conductivity at $f = 10^{-1}$ Hz for PPO/Fe@C60(1%) (\square), PPO/C60(1%) (\circ) samples

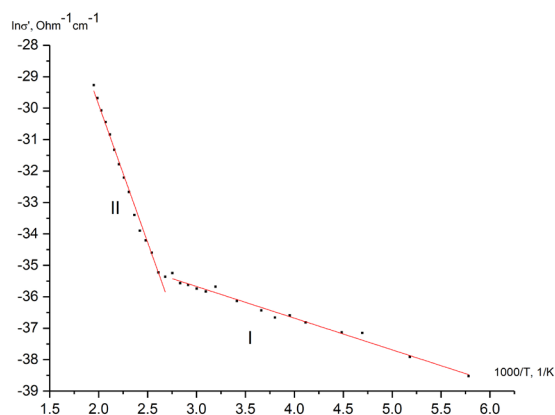


Fig. 4. Temperature dependence of specific conductivity at $f = 10^{-1}$ Hz for pure PPO

Conclusion

The article focuses on the processes of electric charge transfer in quasi-stationary electric field (in the low-frequency range) in the samples of fullerene-containing polyphenylene oxide. The research has revealed two logarithmic dependences of conductivity on the inverse temperature. Each of them corresponds to one of the two conductivity stages. The first conductivity stage with a lower activation energy characterizes intermolecular charge transfer, while the second stage (with a higher activation energy) corresponds to intramolecular transfer. The existence of temperature regions of metallic conductivity was found in composites with endometallofullerene and with high concentration of fullerene (8% C_{60}).

References

- Biryulin, Y. F., Melenevskaya, E. Y., Mikov, S. N. et al. (2003) Optical properties of polydimethylphenyleneoxide free-standing films containing fullerene. *Semiconductors*, 37 (1), 108–111. DOI: 10.1134/1.1538548 (In English)
- Cha, D. H., Kim, H.-J., Hwang, Y. et al. (2012) Fabrication of molded chalcogenide-glass lens for thermal imaging applications. *Applied Optics*, 51 (23), 5649–5656. DOI: 10.1364/AO.51.005649 (In English)
- Jonscher, A. K. (1996) *Universal relaxation law*. London: Chelsea Dielectrics Press, 415 p. (In English)
- Polotskaya, G. A., Lebedev, V. T., Gofman, I. V., Vinogradova, L. V. (2017) Composite films based on polyphenylene oxide modified with endofullerenes C_{60} with encapsulated iron atoms. *Russian Journal of Applied Chemistry*, 90 (9), 1549–1557. DOI: 10.1134/S1070427217090270 (In English)
- Polotskaya, G. A., Penkova, A. V., Toikka, A. M. et al. (2007) Transport of small molecules through polyphenylene oxide membranes modified by fullerene. *Separation Science and Technology*, 42 (2), 333–347. DOI: 10.1080/01496390600997963 (In English)