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

***Abstract.*** The article views 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). Transfer processes connected with intramolecular and intermolecular conductivity have been revealed. It is determined 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, the focus of research has been made on the development of polymeric composite materials (PCM) with high dielectric permittivity which 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 for 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 receive have specific attention as polymer modifiers. Our preceding work was limited by the study 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.%) provided the required amounts of fillers. Thus obtained, the solution was left for 3-4 days to receive 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 40° and dried in vacuum at 40°C up to constant weight (Biryulin, Melenevskaya, Mikov et al. 2003).

The surface morphology and composition of the samples were 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 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. The dielectric measurements were performed in the temperature range between -100$^{o}$C and 250$^{o}$C at $10^{-1}$ Hz and at applied voltage 1.0 V.

**[Fig. 1 should be here]**

## Results and discussion

Specific conductivity or its reciprocal value – the specific electrical resistance of the 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 et al. 2017).

Temperature dependences of natural logarithm of the real part of the complex conductivity $\sigma'$ at $10^{-1}$ Hz for PPO/$C_{60(8\%)}$, PPO/$C_{60(1\%)}$, and pure PPO are given in Figures 2, 3, and 4 respectively. These dependences show two temperature range which can be approximated by straight lines corresponding to Arrhenius equation (Jonscher 1996):

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

where $\sigma'_0$ – pre-exponential factor,

$E_a$ – conductivity activation energy.

**[Fig. 2 should be here]**

**[Fig. 3 should be here]**

**[Fig. 4 should be here]**

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 1. The error in the activation energy values assessment does not exceed 4.5%.

**[Table should be here]**

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

When transferred intramolecularly, the electrons can “jump” from atom to atom, provided these atoms have electron orbitals with the equal energy values. In case the molecules overlap, the electrons move from macromolecule to macromolecule. The first conductivity stage with a lower activation energy values is specific for the intermolecular charge transfer (range II), while a higher activation energy values correspond to intramolecular charge transfer (range I).

Figure 2 shows that for temperatures 60–130°C the specific conductivity for PPO/$C_{60(8\%)}$ (the highest concentration of $C_{60}$ in composite) increases when a temperature decrease. 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 leads to change in the type of conductivity from semiconductor to metallic. The existence of fullerene regions sequences is clearly shown in Figure 1, where the black areas are clusters of $C_{60}$ molecules.

Moreover, the region of metallic conductivity is observed in the samples of fullerene PPO/Fe@$C_{60(1\%)}$ with the embedded iron atoms (Figure 3) at temperatures below 60°C, which is due to clearly displayed metallic properties of iron. The samples which don’t contain iron in the fullerene frame, like PPO/$C_{60(1\%)}$ (Figure 3) and the pure PPO (Figure 4), are only characterized by the semiconductor type of conductivity in the temperature range t = -100 - 250°C. At temperatures above 170°C, 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@$C_{60}$ samples is the result of the conduction electrons concentration growth 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.

## Conclusion

In the article, the processes of electric charge transfer in a quasi-stationary electric field (in the low-frequency range) in the samples of fullerene-containing polyphenylene oxide are analyzed in the article. Two parts in logarithmic dependences of conductivity on inverse temperature are revealed. Each of the part 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% $C_{60}$).

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

Fig. 2. Temperature dependence of specific conductivity at low frequency ($f$=$10^{-1}$Hz) for PPO/$C_{60(8\%)}$ system

Fig. 3. Temperature dependence of specific conductivity at $f$=$10^{-1}$Hz for PPO/Fe@$C_{60(1\%)}$ (□), PPO/$C_{60(1\%)}$ (○) samples

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

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

| Samples | $E_{aI}$, eV | $E_{aII}$, eV | $\sigma_{0I}$, $Ohm^{-1}cm^{-1}$ | $\sigma_{0II}$, $Ohm^{-1}cm^{-1}$ |
|---|---|---|---|---|
| PPO | 0.086 | 0.75 | $6.6*10^{-15}$ | $4.12*10^{-6}$ |
| PPO/$C_{60(1\%)}$ | 0.079 | 1.367 | $3.07*10^{-16}$ | 0.488 |
| PPO/$C_{60(8\%)}$ | 0.28 | 1.17 | $9.6*10^{-12}$ | 0.057 |