Influence of endometallofullerene on the conductive characteristics of polyphenylenoxide

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Abstract. The paper investigates endometallofullerene impact on conductive characteristics of poly(phenyleneoxide) within a wide range of frequencies and temperatures. It is revealed that the introduction of iron into the polymer matrix leads to an increase in the specific conductivity of the material and changes the parameters of its temperature dependence. The revealed regularities can be accounted for electro-donor properties of iron embedded in fullerene molecules.

1. Introduction

Polymers are considered as ideal matrices for the development of new materials that possess desired properties and can be used to produce membranes of broad application, namely, when concentrating and separating suspensions, purifying products from impurities, regenerating valuable components to be reused, obtaining desalinated and purified water, etc.

The object of the present research is polyphenylenoxide (PPO) modified by endometallofullerene C_{60}-Fe that is introduced into the polymer matrix. To date, endohedral carbon clusters (endometallofullerenes) that contain metal atoms inside a fullerene molecule are fullerene derivatives that are becoming an intensive and promising field of research.

Endometallofullerenes (EMF) represent a completely new type of carbon clusters that are distinctively different from hollow fullerenes. The metal atom embedded inside a fullerene molecule changes its electronic properties significantly. However, research into the properties of these derivatives is still limited due to challenges in synthesis, low output of the material and poor solubility as well as extremely high production costs. Nevertheless, due to its magnetic properties, given it is introduced inside the fullerene molecule iron is extremely promising for enhancing polymer conductivity and development of new materials with specific properties: superconductors, organic ferromagnetics, laser and ferroelectric materials, pharmaceuticals.

2. Experimental

The paper presents the results of studies of dielectric and conductive characteristics of polyphenylenoxide (PPO) composites with 1% content of fullerene C_{60} samples and those of composite PPO + 1% EMF Fe-C_{60}.

The composites were obtained by mixing solutions of PPO in chloroform (concentration 2 wt.%) and fullerene C_{60}/endofullerene C_{60}-Fe in toluene (concentration 0.14 wt.%) in the amounts that provide the desired filler content in the composite. The solution obtained in this manner was left for 3-
4 days for interaction between the polymer and the fullerene molecules to take place. 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 the method of toluene evaporation from the mixture the polymer and the filler on the surface of cellophane at a temperature of 40°C. [1]

The measurement of the dielectric spectra was conducted on the spectrometer "Concept 81" produced by the company NOVOCONTROL TechnologiesGmbH& Co with the automatic ALPHANB high performance frequency analyzer. The samples were thin layers with a thickness of 60-125 microns and a diameter of 15 mm. The measurement of the parameters of the PCM samples was performed in the temperature range from 273 K to 523 K and within the range of frequencies between $5 \times 10^{-2}$ and $1 \times 10^{6}$ Hz. The voltage applied to the sample equalled 1.0 V.

3. Results and discussions

Frequency dependence of the complex conductivity $\sigma'(f)$ in the range $10^{-1} - 10^{6}$ obtained for the films of the systems at temperatures of T=273K...523К indicates growth of $\sigma'(f)$ with an increase in frequency. The transition from the frequency-independent zone to the frequency-dependent one was identified, which indicates the beginning of conductivity relaxation.

![Figure 1](image-url)  
**Figure 1.** The dependence of sample PPO+1%C_{60} conductivity on frequency in the external field at different temperatures.

The comparison of the spectra of PPO+C_{60} (Figure 1) and PPO+C_{60} -Fe (Figure 2) samples showed an increase in conductivity that is ten-fold times much within the whole frequency interval, which can be a cause for clearly observed electron-donor properties of iron embedded in the fullerene matrix. Thus, EMF not only display obvious electron-acceptor properties, like hollow fullerene, but also demonstrate properties of electron-donors.

According to the current experimentally-based conception, electrical conductivity in polymeric dielectrics is mainly of ionic character. It is known that alternating current conductivity for amorphous semiconductors is expressed as [2]:

$$\sigma' = \sigma_{ac} (\omega) = \sigma_r (\omega) - \sigma_{dc} (\omega) = A \omega^s,$$

where $\omega$ is angular frequency ($\omega = 2\pi f$ – test frequency), $\sigma_r (\omega)$ – measured total conductivity, $\sigma_{dc} (\omega)$ – conductivity measured at constant current, $s$ is an exponent and $A$ is a constant that is dependent on temperature.
Figure 2. The dependence of conductivity of PPO+1%C₆₀−Fe sample on frequency in the external field at different temperatures.

Values of the exponent s were calculated for the samples under investigation by nonlinear approximation of the experimental curves (Figure 3).

Figure 3. The dependence of the exponent s on temperature for the studied systems.

It was found out that s decreases with an increase in temperature in the range between 1 and 0.5, which can be regarded as experimental confirmation that conductivity is provided by hopping mechanism. It is assumed that in the model of hopping mechanism with accidental energy value [3] the elementary act of polarization is the overbarrier transition of one carrier from one state into another, and the activation energy of the center is caused by Coulomb’s interaction.
The temperature dependence of the specific conductivity $\sigma'$ on various frequencies has also been investigated for the studied samples.

**Figure 4.** The dependence of the conductivity of PPO+1%$C_{60}$–Fe sample on temperature for different frequencies in the external field.

**Figure 5.** The dependence of the conductivity of PPO+1%$C_{60}$ sample on temperature for different frequencies in the external field.

Figure 4 shows the graph of $\sigma'$ dependence on $1000/T$ of the sample PPO+1%$C_{60}$–Fe at temperatures $T=173$K...523K. As it can be seen from the figure, this dependence has a complex character with the zone of exponential dependence, according to Arrhenius's law. In the zone of high temperature, nonlinear increase in $\sigma'$ along with the growth of temperature was revealed.

Multiple regions of the exponential dependence and the changing nature of temperature dependence for PPO+1%$C_{60}$-Fe samples in Figure 5 can be caused by either the presence of impurities and defects in the sample structure or by transition process from mixed conductivity to ionic conductivity.
Apparently, at low temperatures, the source of free charges that are non-bound chemically with macromolecules is ionic impurities with low molecular weight, the mobility of which is limited by high viscosity of the medium. At high temperatures, conductivity becomes intrinsic.

4. Conclusions

The comparison of the spectra of PPO+C60 and PPO+C60 –Fe samples showed an increase in conductivity that is ten-fold times much within the whole frequency interval. It is revealed that the introduction of iron into the polymer matrix leads to an increase in the specific conductivity of the material and changes the parameters of its temperature dependence. It was found out that $s$ decreases with an increase in temperature in the range between 1 and 0.5, which can be regarded as experimental confirmation that conductivity is provided by hopping mechanism. The revealed regularities can be accounted for electro-donor properties of iron embedded in fullerene molecules.

References

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