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Condensed Matter Physics. Dielectrics

UDC 537.9

EDN ZFBEBQ

<https://www.doi.org/10.33910/2687-153X-2023-4-2-47-52>

Thermoactivational spectroscopy of polyethylene polymer films with an ethylene-vinyl acetate copolymer

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For citation: Galikhanov, M. F., Karulina, E. A., Fomicheva, E. E., Reztsov, T. V. (2023) Thermoactivational spectroscopy of polyethylene polymer films with an ethylene-vinyl acetate copolymer. *Physics of Complex Systems*, 4 (2), 47–52. <https://www.doi.org/10.33910/2687-153X-2023-4-2-47-52> EDN ZFBEBQ

Received 30 March 2023; reviewed 21 April 2023; accepted 21 April 2023.

Funding: This study was supported by the Ministry of Education of the Russian Federation as part of the state-commissioned assignment (project No. VRFY-2023-0005).

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Abstract. The article reports the results of the study of polymer films based on the blend of high-pressure polyethylene (LDPE) and the ethylene-vinyl acetate copolymer (EVA, sevilen). The films were investigated with thermally stimulated depolarization. It is noted that one maximum is observed on the temperature dependences of the depolarization currents obtained for samples with different sevilen content. It is assumed that this maximum corresponds to the dipole-segmental relaxation that occurs in high-pressure polyethylene. Calculation results of activation energies corresponding to this process allow us to conclude that an increase in the proportion of EVA in the blend leads to an increase in the dipole-segmental mobility and, as a consequence, to an increase in the flexibility of the polymer.

Keywords: polyethylene, ethylene-vinyl acetate copolymer, thermally stimulated depolarization, thermoactivational spectroscopy, dipole-segmental relaxation

Introduction

Today, new ways of using polyolefins in various fields of technology are emerging. One of the areas of polymer dielectrics application is the creation of electrets. Electrets are dielectrics which create a strong electrostatic field in the surrounding space as a result of their polarization. They are used in the production of electroacoustic and electromechanical transducers and electret air filters. Also, electrets are used in medicine and industrial applications as active packaging materials, etc. This can be achieved by changing the structure of the polymer or the composition of the copolymer matrix.

One typical representative of polyolefins is polyethylene, e.g., high pressure polyethylene (LDPE). It is a non-polar polymer that has fairly good dielectric properties due to the structure of its macromolecules. It is characterized by a low permittivity, high electrical resistivity, and high dielectric strength.

However, according to (Burda 2013) and (Gorokhovatskij 2009), LDPE has a rather short electret state lifetime. Nevertheless, it should be noted that this material has good mechanical properties.

It is also relatively cheap to manufacture and, therefore, is widely used in technology, medicine and other sectors. Hence, increasing the stability of the electret state in LDPE films holds promise.

In recent years, structural parameters and external conditions that affect electret properties of polyethylene have been actively studied (Galikhanov et al. 2009; 2017; Shkuro et al. 2012).

Today, targeted improvement of the physicochemical properties of a polymer is achieved through using the modification method. It is based on the creation of polymer-polymer compositions. One of the frequently used polymer blends in the manufacturing of such compositions is the combination of polyethylene and an ethylene-vinyl acetate copolymer. Mixing different types of polymers with sevilen is widely used to change mechanical and electrical properties of polymers (Ableev et al. 2016; Baulin et al. 2015; Mishak et al. 2007).

EVA (sevilen) is a polar polymer whose polarity is determined by the presence of vinyl acetate. It is known that as the content of vinyl acetate increases, the flexibility and strength of sevilen improve at low temperatures. This makes it an appropriate material for active packaging for frozen foods (Stepanov et al. 2015). Elastic electrets can be used not only as active packaging, but also in soft electronics, such as pulse wave or heartbeat sensors and tactile control devices (Baulin et al. 2015; Mishak et al. 2007).

Considering the relevance of studies in elastic electret polymers, an ethylene-vinyl acetate copolymer may turn out to be an appropriate material. Despite the fact that the electret properties of savilene have been thoroughly described (Galikhanov 2006; Galikhanov, Budarina 2002), it is still not completely clear how the percentage of EVA in the structure of the LDPE copolymer affects its electrophysical parameters.

In this regard, the purpose of this work is to investigate the effect of the percentage of EVA in the composite modification with LDPE on the electrical properties of LDPE.

Samples and research methods

The study focused on the blends of high-pressure polyethylene with an ethylene-vinyl acetate copolymer of different ratio of components. The film samples have a thickness of about 300 μm .

The blending of polymers is carried out on laboratory microrollers at a temperature of 130 ± 5 °C. The blending time is 3 minutes. The films are prepared by pressing at a temperature of 170 ± 5 °C. The holding time under pressure is 5 minutes. Samples of blends of LDPE and EVA are provided by the Kazan National Research Technological University.

The method of thermally stimulated depolarization (TSD) is chosen as the main research method. The essence of the method lies in the polarization of the sample during its cooling and further measurement of currents when the samples are heated. The polarization of the sample is carried out at a temperature above the glass transition temperature (Sazhin et al. 1986), followed by a temperature decrease with turned on field. In this case, the orientation of the dipoles is frozen. Heating the sample leads to an increase in the molecular mobility of the dipoles. As a result, while the sample is heated, a depolarization current flows through it. This current corresponds to relaxation transitions, which appear as maxima in the depolarization spectrum (Gorokhovatskij, Bordovskij 1991; Sessler 1983).

In the study, thermally stimulated currents are measured on a TSC-II (Setaram). Resolution for measuring current is 10^{-16} A. Operating temperatures range is from -150 °C to 250 °C. Temperature measurement error is 0.1 °C. The samples are polarized by the contact method by applying an electric field of 100 V/mm for 2 minutes at a temperature of 40 °C, after which they are cooled at a rate of 2 °C/min to 0 °C in the applied field. The studies are carried out at heating rates of 3 °C/min, 7 °C/min, 9 °C/min.

The activation energy is calculated by varying the heating rate (Gorokhovatskij, Bordovskij 1991). Depolarisation curves are obtained at two sample heating rates. Based on them, the energy distribution functions of electrically active defects are constructed, which make it possible to estimate the activation energy.

Experimental results and discussion

The TSD spectra show one process (Fig. 1) represented as a maximum. Its position depends on the ratio of components in the blend. When increasing the EVA percentage, the maximum shifts to lower temperatures and its height decreases. The dependence of the temperature position of the maximum peak on the EVA percentage is described by a linear dependence (Fig. 2).

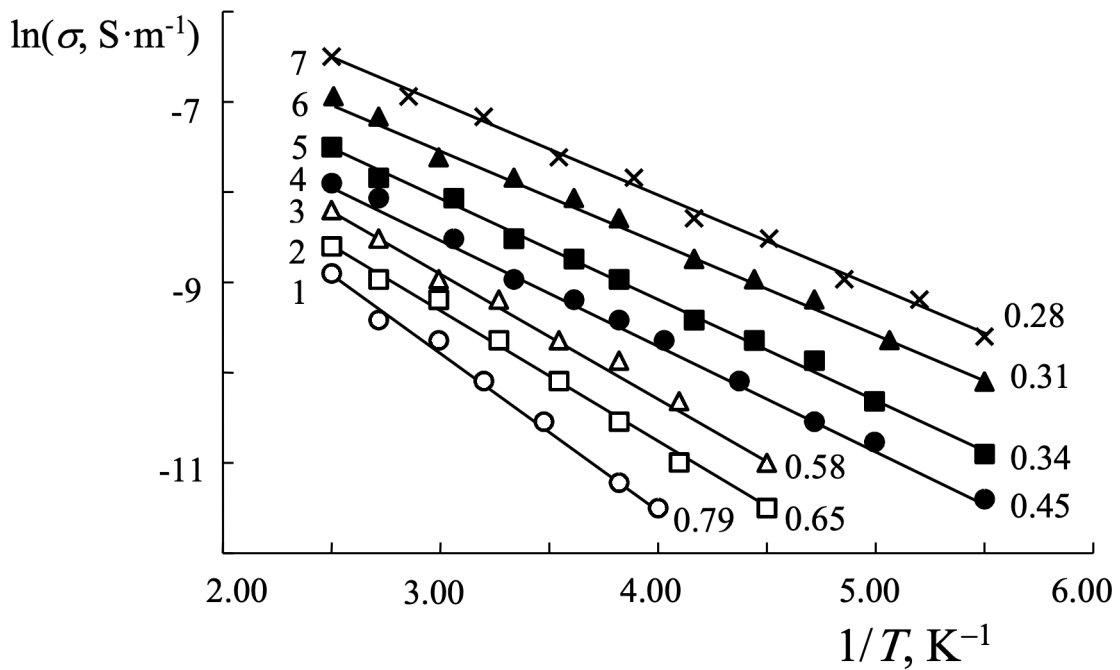


Fig. 1. The temperature dependences of the depolarization currents obtained for samples of the LDPE-EVA with different EVA percentages

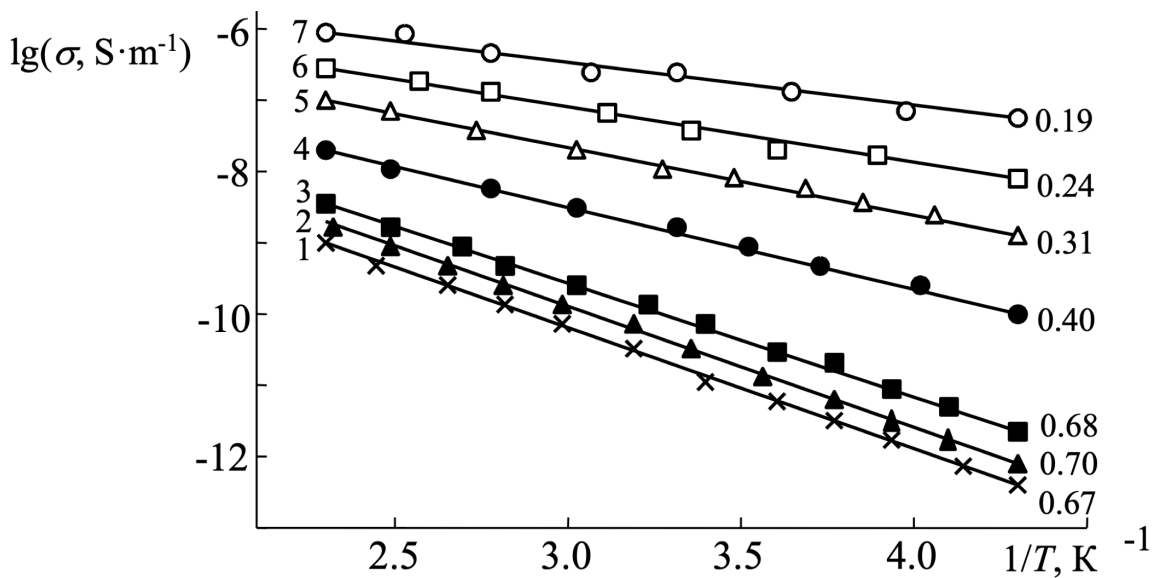


Fig. 2. The dependence of the temperature position of the maximum on the EVA percentage in the blend

It is known (Ellis, Smith 2008) that dipole-segmental relaxation (α -relaxation) is observed in polyethylene between 40 and 50 °C. As is said before, polyethylene is a nonpolar polymer. However, it contains polar carbonyl groups $C = O$ and the dielectric relaxation occurs due to them (Sessler 1983).

Extrapolation of the straight line describing the shift of the peak position to the region where the EVA percentage tends to zero indicates a temperature around 40 °C (Fig. 2). It can be assumed that the maximum observed in Fig. 1 corresponds to the process of charge accumulation and relaxation occurring in polyethylene. An increase in the EVA percentage in the blend leads to a shift of this process to lower temperatures. In this case, the number of relaxers in polyethylene decreases and their mobility is facilitated.

The area under the plot of current versus time for the TSD spectra is calculated. It corresponds to the charge released during relaxation. In the case of dipole-segmental relaxation, this is evidence in favor of the rotation of chain segments. The decrease in the peak area indicates the decrease in the amount of relaxers in the blend and also confirms that polyethylene is responsible for the presence of the peak in the TSD spectrum (Fig. 3).

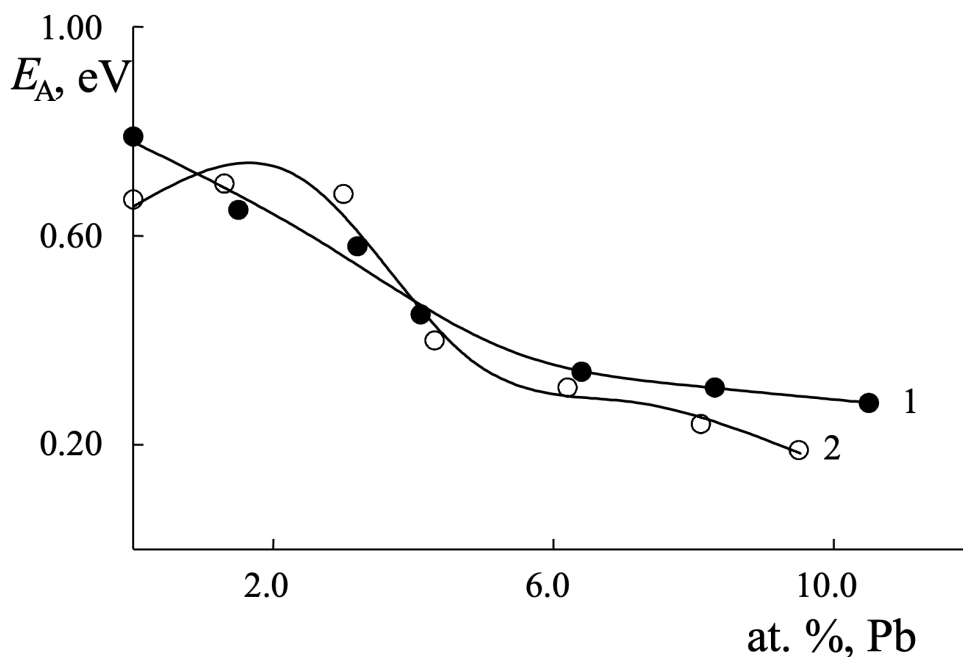


Fig. 3. The dependence of the area under the graphics on the EVA percentage in the blend

The process observed on the depolarization currents spectra has a thermally activated origin. As the sample heating rate increases, the maximum shifts towards higher temperatures (Fig. 4).

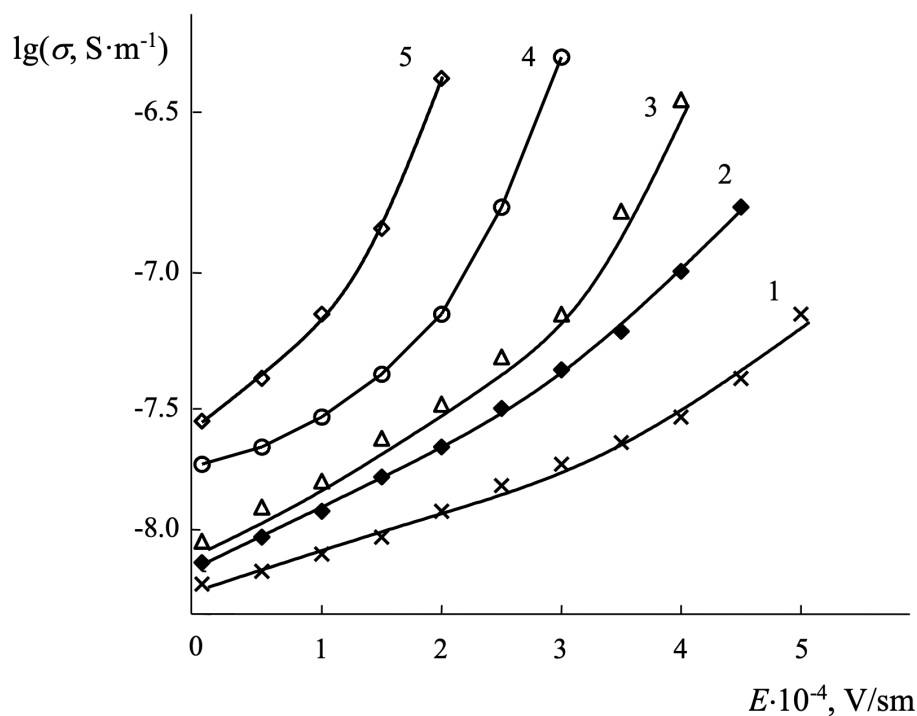


Fig. 4. The temperature dependences of the depolarization currents obtained for samples with the same EVA percentage (70%) but at different heating speeds: 1—7 °C/min, 2—9 °C/min

By measuring the depolarization currents for several heating rates, the activation energy corresponding to electrically active defects in these samples can be estimated. The activation energies calculated by the method of varying the heating rate are shown in Table 1.

Table 1. The dependence of the activation energy on the EVA percentage in the copolymer

The EVA percentage, %	The activation energy, eV
30	0.52
40	0.50
50	0.50
60	0.46
70	0.45
80	0.35
90	0.33

With an increase in the percentage of EVA in the blend, a slight decrease in the values of the activation energy is observed. This fact indicates that the mobility of the chain segments is facilitated and the polymer becomes more flexible.

It is known from (Ellis, Smith 2008) that with a change in the degree of crystallinity of the polymer, the maximum temperature of the peak corresponding to α -relaxation shifts at a practically constant activation energy. The behavior of the peak in the TSD spectra of the blend of LDPE and EVA is similar to the data analyzed in (Sazhin et al. 1986). This may be another confirmation that α -relaxation is the reason for the appearance of this maximum in the TSD spectra.

Conclusions

The study demonstrates that there is one maximum in the spectra of thermally stimulated depolarization of LDPE and EVA blends. Its presence may be associated with the relaxation processes occurring in polyethylene. The depolarization current maximum shifts to the region of lower temperatures with an increase in the EVA percentage. In this case, the area of the maximum decreases.

It has been suggested that this process is associated with dipole-segmental relaxation in polyethylene due to the presence of carbonyl groups in the crystalline region of the polymer. A decrease in the peak area in the TSD spectrum with an increase in the percentage of EVA in the blend confirms that the process occurring in polyethylene is the reason for the appearance of the maximum.

It has been established that the activation energy corresponding to this process decreases with an increase in the EVA percentage in the blend. Therefore, an increase in the EVA percentage facilitates dipole-segmental mobility and the polymer becomes more flexible. Blends of increased flexibility may find an application in production processes that use flexible polymers.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors discussed the final work and took part in writing the article.

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