

DOI: 10.18721/JPM.13201

UDC: 538.9

ELECTRIC CHARGE RELAXATION IN THE POLYETHYLENE WITH MINERAL INCLUSIONS OF DIATOMITE

Yu.A. Gorokhovatsky, N.S. Demidova, D.E. Temnov

Herzen State Pedagogical University of Russia, St. Petersburg, Russian Federation

The paper considers methods for increasing stability of polyethylene's electret state by adding diatomite particles to its composition. The results of analyzing the IR spectra, the involved materials' temporal and temperature stability are presented. Mechanisms for improving the stability of the composite polyethylene's electret state are discussed.

Keywords: electret state, polyethylene, diatomite, thermoactivation spectroscopy

Citation: Gorokhovatsky Yu.A., Demidova N.S., Temnov, D.E. Electric charge relaxation in the polyethylene with mineral inclusions of diatomite, St. Petersburg Polytechnical State University Journal. Physics and Mathematics. 13 (2) (2020) 9–15. DOI: 10.18721/JPM.13201

This is an open access article under the cc by-nc 4.0 license (<https://creativecommons.org/licenses/by-nc/4.0/>)

РЕЛАКСАЦИЯ ЭЛЕКТРИЧЕСКОГО ЗАРЯДА В ПОЛИЭТИЛЕНЕ С МИНЕРАЛЬНЫМИ ВКЛЮЧЕНИЯМИ ДИАТОМИТА

Ю.А. Гороховатский, Н.С. Демидова, Д.Э. Темнов

Российский государственный педагогический университет им. А.И. Герцена,
Санкт-Петербург, Российская Федерация

В работе рассматриваются методы повышения стабильности электретного состояния полиэтилена путем добавления в его состав частиц диатомита. Приводятся результаты исследования ИК-спектров, временной и температурной стабильности исследуемых материалов. Обсуждаются механизмы улучшения стабильности электретного состояния композитного полиэтилена.

Ключевые слова: электретное состояние, полиэтилен, диатомит, термостимулированная спектроскопия

Ссылка при цитировании: Гороховатский Ю.А., Демидова Н.С., Темнов Д.Э. Релаксация электрического заряда в полиэтилене с минеральными включениями диатомита // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2020. Т. 13 2 №. С. 9–16. DOI: 10.18721/JPM.13201

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>)

Introduction

Polyethylene is one of the most widely used polymeric materials. At the moment, the polyethylene's electret properties are studied to create the active packages. One of the ways to increase the electret state stability is the creation of the composite material [1, 2]. Studies performed in Ref. [3] showed that adding aerosil in polyethylene leads to a significant improvement in the electret state stability of the obtained composite material. Aerosil is a very pure amorphous non-porous silicon dioxide with a particle size of 5 to 40 nm. Diatomite is another modification of silica. Diatomite is a more promising material for creating composites based on polyethylene because of its low cost.

In the work, the electret stability of composite polyethylene with diatomite has been compared with pure polyethylene films' stability using various methods.

We used such methods as thermostimulated potential relaxation, isothermal potential relaxation, depolarization with registration of short-circuit currents of a pre-charged dielectric and IR spectroscopy. The film thickness was about 1 mm.

Experimental technique

Samples were made by rolling and subsequent pressing. The Kazan National Research Technological University equipment was used. High pressure polyethylene, the brand 15313-003, GOST 7699-78 was used for creating the composite material. Mixing of the starting polyethylene with the filler was carried out in a mixing chamber. The mixing chamber consisted of 2 half cylinders containing horizontally rotating rolls. For the better distribution of filler particles, the rolls rotated in the opposite directions and had different rotation speeds. The temperature in the mixing chamber was 420–430 K.

The films were created using the pressing method in accordance with GOST 12019-66. The mold was a frame between two polished plates. Lavsan film was used to prevent the pressed sample's adhesion to the mold plates. The mold with the composite material was placed between the cooling plates, which, in turn, were placed between the heated plates. After the sample heating, the press plates were closed to create the necessary pressure and withstood the necessary time. After that, the samples were cooled by water, then the pressure was removed from the plates, the press was opened and the samples were removed.

Diatomite distribution was monitored using a Nikon Eclipse LV150 optical microscope. IR spectra were obtained by means of a FSM 1202 Fourier spectrometer. When studying the electret state stability by the isothermal and thermally stimulated potential relaxation methods, the films were polarized in a corona discharge at 5 kV.

Electrically active defects' activation energy was calculated using the Tikhonov regulatory algorithms.

Experimental results and discussion

Our study of the composite materials without treatment did not show a significant effect of diatomite on their electret properties. Earlier it had been shown that the main mechanism of deterioration the polyethylene's electret properties was the presence of water molecules in it [4 – 7]. Diatomite, being a natural mineral, also contains water, which can impair the composite's electret properties. To reduce the amount of physically absorbed water in the composite structure, before studying the properties, samples were annealed in a muffle furnace for 1 h at a temperature $T = 400$ K.

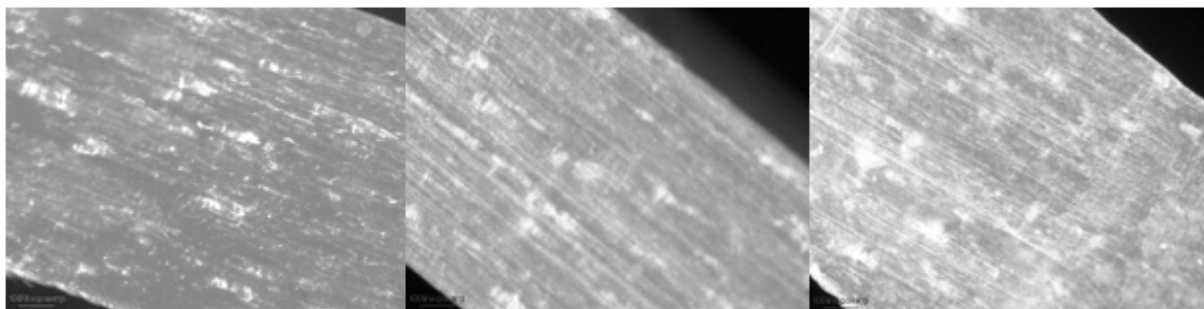


Fig. 1. Optical images of slices of the polyethylene films including diatomite; a filler content (% vol.) is 2 (left), 4 (in the center) and 6 (right)



Fig. 2. IR transmission spectra of LDPE (1) and of the composite of LDPE + 6 % diatomite (2). The presence of water is highlighted

The addition of diatomite to polyethylene leads to its gray color, so that the distribution of the filler in the polyethylene film can be controlled optically.

Fig. 1 shows the optical images of polyethylene film's slices with a diatomite concentration of 2, 4, and 6 % vol. Analysis of the filler distribution showed a uniform pattern of diatomite in the polyethylene film.

The optical spectroscopy method is highly effective in studying the physical and physicochemical properties of water-containing polymer objects [8 – 10]. Fig. 2 shows the infrared (IR) transmission spectra of the initial *low density polyethylene* (LDPE) and composite polyethylene with 6 % diatomite. Absorption bands in the region of 1500–1650 cm^{-1} are associated with the presence of water dissolved in the polymer. These

spectra show the presence of water in the initial LDPE film and its substantial decrease with the addition of diatomite (see Fig. 2).

In order to study directly the electret state stability in the composite polyethylene, the films were investigated by the isothermal potential relaxation method at a temperature of 343 K. The films were polarized in a corona discharge at 5 kV for 360 s. The polarization temperature was 360 K.

Fig. 3 shows the time dependence of the electric potential relaxation for films of pure polyethylene and polyethylene with the different diatomite content. The graphs show a significant increase in the stability of polyethylene films when diatomite is introduced into their composition.

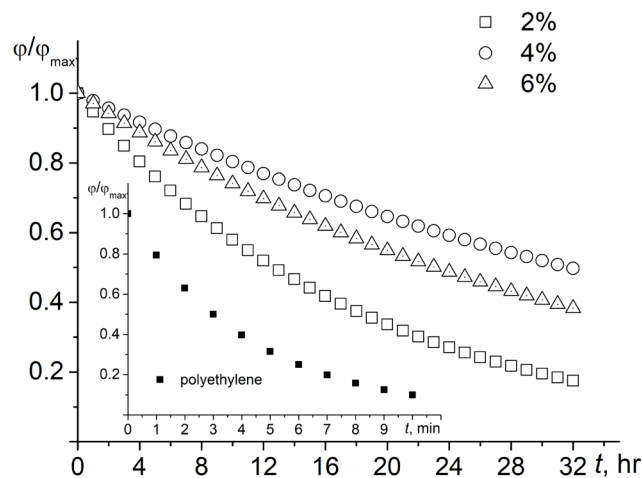


Fig. 3. The time dependences of the surface potential relaxation for pure polyethylene film (in the inset) and composite polyethylene with the different diatomite content

The diatomite adding into the polyethylene films leads to the stability increasing that it is obvious from the spectra obtained by thermostimulated potential relaxation method (Fig. 4). The thermally stimulated potential relaxation spectra were obtained both for the unannealed and annealed films of the polyethylene with 4 % diatomite; these curves are compared in Fig. 4. The graphs show a significant improvement of the composite polyethylene film's electret state stability after annealing. Thus, nonannealed films of composite polyethylene with diatomite did not exhibit high electret stability.

The electrically active defects' activation energy is one of the main characteristics of the relaxation process of electric charge decay [11]. To calculate this parameter, the study of pure and composite polyethylene was carried out by the method of thermally stimulated depolarization (TSD). A TSC-II setup by Setaram (France) was used for measurements. Sensitive electrometer Keithley 6517 is the main measuring device of the setup. The thermostimulated currents were measured in the temperature range between 290 and 380 K at the fixed heating rate. The heating rate was from $5 \cdot 10^{-2}$ to $1,5 \cdot 10^{-1}$ K/s. The samples

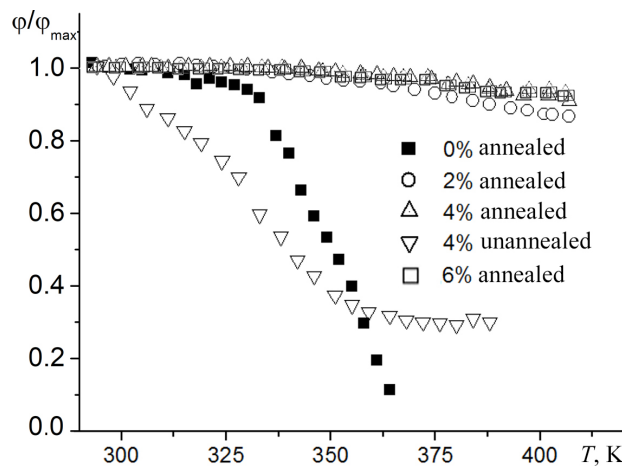


Fig. 4. The temperature dependences of the surface potential relaxation for the pure annealed polyethylene films and the composite polyethylene (unannealed and annealed) with the different diatomite content

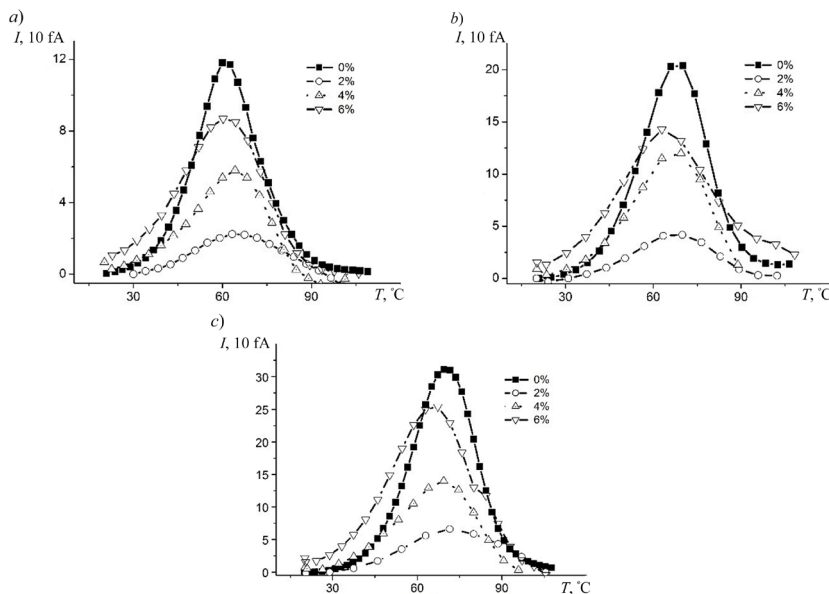


Fig. 5. Thermally stimulated depolarization spectra of the pure polyethylene films and of the composite polyethylene ones with diatomite. The heating rates (K/s) were $5 \cdot 10^{-2}$ (a), $1,0 \cdot 10^{-1}$ (b) and $1,5 \cdot 10^{-1}$ (c). For pure polyethylene films, the current value was reduced by 10 times



were polarized in the electric field $E = 500$ V/mm at a polarization temperature $T_p = 343$ K, during a polarization time of 300 s. After the electric field exposure for 300 s, the samples were cooled in the applied field with a rate of $3,3 \cdot 10^{-2}$ K/s up to 293 K. The thermostimulated currents' spectra are shown in Fig. 5.

TSD data were processed using Tikhonov's regularizing algorithms. Fig. 6 shows the reconstructed distribution functions of the electrically active defects. It can be seen from the graphs that the maxima shift towards the higher energy and the distribution broadens with increasing the diatomite concentration. Table shows the values of the electrically active defects' activation energy for all the compositions. The activation energy value obtained in this work for electrically active defects for polyethylene without filler is in good agreement with the results of our previous studies [12].

Summary

Our study showed that the creation of composite polyethylene based on diatomite could increase the electret stability of LDPE. The adding diatomite to polyethylene leads to increasing the charge traps' activation energy, at least up to a concentration of 6 vol%. Diatomite can be used for creating composite polyethylene to increase its electret stability in order to create active packages. It is important to continue further studies of the electret stability of polyethylene composite films with a higher concentration of diatomite and to study other fillers containing silicon dioxide.

The research was supported by the Russian Foundation for Basic Research (Grant No. 19-32-90271) and the Ministry of Science and Higher Education of the Russian Federation (Project No. FSZN-2020-0026).

Table
The values of the electrically active defects' activation energy for pure and composite LDPE films

Diatomite concentration, % vol.	Activation energy, eV
0	1.1 ± 0.1
2	1.4 ± 0.1
4	2.2 ± 0.2
6	2.6 ± 0.3

Footnote. Tikhonov's regularizing algorithms were used.

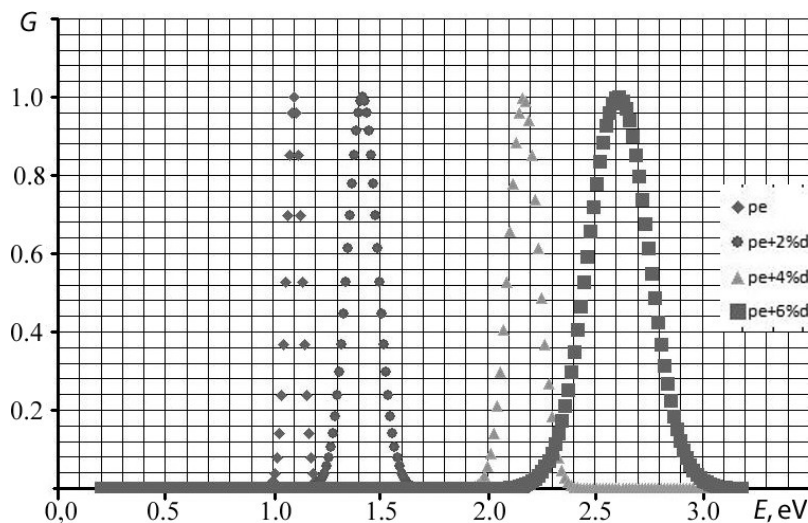


Fig. 6. The energy distribution functions of electrically active defects in the pure polyethylene (pe) and the composite one with the different diatomic (d) content (% vol.)

REFERENCES

1. **Goldade V.A.**, Electret composite materials based on polymers: Main properties and new fields of application, *Mechanics of Composite Materials*. 34 (2) (1998) 107–114.
2. **Gorokhovatsky Yu., Temnov D.**, Electret state in composite polymer materials based on low density polyethylene and polypropylene, *Applied Mechanics and Materials*. 752–753 (April) (2015) 225–231.
3. **Temnov D., Fomicheva E., Tazekov B., et al.**, Electrets properties of polyethylene films with starch and aerosol, *Journal of Materials Science and Engineering A*. 3 (7) (2013) 494–498.
4. **Bordovsky G.A., Gorokhovatsky Y.A., Temnov D.E.**, Electret properties of polyethylene films with nano-dimension inclusions of SiO₂, *Scientific Papers of the Institute of Electrical Engineering Fundamentals of Wroclaw Technical University Conferences*. (2007) 194–197.
5. **Guzhova A.A., Galikhanov M.F., Gorokhovatsky Y., et al.**, Improvement of polylactic acid electret properties by addition of fine barium titanate, *Journal of Electrostatics*. 79 (February) (2016) 1–6.
6. **Kreuer K.D.**, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, *Journal of Membrane Science*. 185 (1) (2001) 29–39.
7. **Shim W.S., Lee Y.H., Yeo I.H., et al.**, Polypyrrole/thermally sensitive polyelectrolyte composite, *Synthetic Metals*. 104 (2) (1999) 119–127.
8. **Okumura S., Nakashima S.**, Water diffusivity in rhyolitic glasses as determined by in situ IR spectroscopy, *Physics and Chemistry of Minerals*. 31 (3) (2004) 183–189.
9. **Kitano H., Nagaoka K., Tada S., et al.**, Structure of water incorporated in amphoteric polymer thin films as revealed by FT-IR spectroscopy, *Macromolecular Bioscience*. 8 (1) (2008) 77–85.
10. **Karulina E.A., Temnov D.E., Chistyakova O.V., Demidova N.S.**, The study of the sorbed water content in composite polymers by Fourier spectroscopy, “Physics of Dielectrics (Dielectrics-2017)”, *Proceedings of the 14-th International Conference* (2017) 35–37.
11. **Sessler G.M.** (Ed.), *Electrets (Topics in Applied Physics, Vol. 33)*, Second Ed., Springer-Verlag, Berlin, Heidelberg, 1987.
12. **Gorokhovatsky Yu., Temnov D.**, Thermostimulated relaxation of surface potential and thermostimulated discharge currents in dielectrics, *Izvestia of Herzen State Pedagogical University*. (8(38)) (2007) 24–34.

Received 04.05.2020, accepted 15.05.2020.

THE AUTHORS

GOROKHOVATSKY Yuriy A.

Herzen State Pedagogical University of Russia
48 Moyka Emb., St. Petersburg, 191186, Russian Federation
gorokh-yu@yandex.ru

DEMIDOVA Natalya S.

Herzen State Pedagogical University of Russia
48 Moyka Emb., St. Petersburg, 191186, Russian Federation
demidov_evg@mail.ru

TEMNOV Dmitry E.

Herzen State Pedagogical University of Russia
48 Moyka Emb., St. Petersburg, 191186, Russian Federation
tde@herzen.spb.ru

СПИСОК ЛИТЕРАТУРЫ

1. **Гольдаде В.А.** Электретные композитные материалы на основе полимеров: основные свойства и новые области применения. // *Механика композитных материалов*. 1998. Т. 34. № 2. С. 153–162.
2. **Gorokhovatsky Yu., Temnov D.** Electret state in composite polymer materials based on low density polyethylene and polypropylene // *Applied Mechanics and Materials*. 2015. Vols. 752–753. April. Pp. 225–231.



3. **Temnov D., Fomicheva E., Tazenkov B., Karulina E., Gorokhovatsky Yu.** Electrets properties of polyethylene films with starch and aerosil // *Journal of Materials Science and Engineering A*. 2013. Vol. 3. No. 7. С. 494–498.
4. **Bordovsky G.A., Gorokhovatsky Y.A., Temnov D.E.** Electret properties of polyethylene films with nano-dimension inclusions of SiO₂ // *Scientific Papers of the Institute of Electrical Engineering Fundamentals of Wroclaw Technical University Conferences*. 2007. Pp. 194–197.
5. **Guzhova A.A., Galikhanov M.F., Gorokhovatsky Y., Temnov D.E., Fomicheva E.E., Karulina E.A., Yovcheva T.A.** Improvement of polylactic acid electret properties by addition of fine barium titanate // *Journal of Electrostatics*. 2016. Vol. 79. February. Pp. 1–6.
6. **Kreuer K.D.** On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells // *Journal of Membrane Science*. 2001. Vol. 185. No. 1. Pp. 29–39.
7. **Shim W.S., Lee Y.H., Yeo I.H., Lee J.Y., Lee D.S.** Polypyrrole/thermally sensitive polyelectrolyte composite // *Synthetic Metals*. 1999. Vol. 104. No. 2. Pp. 119–127.
8. **Okumura S., Nakashima S.** Water diffusivity in rhyolitic glasses as determined by in situ IR spectroscopy // *Physics and Chemistry of Minerals*. 2004. Vol. 31. No. 3. Pp. 183–189.
9. **Kitano H., Nagaoka K., Tada S., Gemmei-Ide M., Tanaka M.** Structure of water incorporated in amphoteric polymer thin films as revealed by FT-IR spectroscopy // *Macromolecular Bioscience*. 2008. Vol. 8. No. 1. Pp. 77–85.
10. **Карулина Е.А., Темнов Д.Ф., Чистякова О.В., Демидова Н.С.** Исследование содержания сорбированной воды в композитных полимерах методом Фурье-спектроскопии // «Физика диэлектриков (Диэлектрики 2017-)». Материалы XIV Международной конференции. СПб., 29 мая – 2 июня 2017 г. Т. 1. СПб.: Изд-во РГПУ им. А.И. Герцена, 2017. С. 35–37.
11. **Сесслер Г.** Электреты. М.: Мир, .1983 487 с.
12. **Гороховатский Ю.А., Темнов Д.Э.** Термостимулированная релаксация поверхностного потенциала и термостимулированные токи короткого замыкания в предварительно заряженном диэлектрике // *Известия РГПУ им. А.И. Герцена. Естественные и точные науки*. 2007. № 8 (38). С. 24–34.

Статья поступила в редакцию 04.05.2020, принята к публикации 15.05.2020.

СВЕДЕНИЯ ОБ АВТОРАХ

ГОРОХОВАТСКИЙ Юрий Андреевич – доктор физико-математических наук, заведующий кафедрой общей и экспериментальной физики Российского государственного педагогического университета им. А.И. Герцена, Санкт-Петербург, Российская Федерация.

191186, Российская Федерация, г. Санкт-Петербург, наб. р. Мойки, 48
gorokh-yu@yandex.ru

ДЕМИДОВА Наталья Сергеевна – аспирантка кафедры общей и экспериментальной физики Российского государственного педагогического университета им. А.И. Герцена, Санкт-Петербург, Российская Федерация.

191186, Российская Федерация, г. Санкт-Петербург, наб. р. Мойки, 48
demidov_evg@mail.ru

ТЕМНОВ Дмитрий Эдуардович – кандидат физико-математических наук, доцент кафедры общей и экспериментальной физики Российского государственного педагогического университета им. А.И. Герцена, Санкт-Петербург, Российская Федерация.

191186, Российская Федерация, г. Санкт-Петербург, наб. р. Мойки, 48
tde@herzen.spb.ru