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Temperature dependence of electrical conductivity during the heating–cooling cycle of gamma-irradiated high-density polyethylene

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TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY DURING THE HEATING–COOLING CYCLE OF GAMMA-IRRADIATED HIGH-DENSITY POLYETHYLENE

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Abstract: The temperature dependence of the alternating current (σ_{ac}) electrical conductivity of a gamma-ray-irradiated high-density polyethylene (HDPE) sample was studied during the heating–cooling cycle, expressed as $\sigma_{ac} = f(T)$. The electrical conductivity of the (initial) pure HDPE sample during the heating–cooling cycle, before irradiation, is related to the mobility of charge carriers (ions) as well as to the charge carriers injected from the electrode. The increase in conductivity resulting from the absorbed radiation dose is due to the formation of additional charge carriers in the sample, while the decrease is attributed to the weakening of bonds between polymer macromolecules caused by the absorbed dose. During the reverse cooling process of an HDPE sample after irradiation, the supramolecular structure of the polymer phase undergoes a significant change as a new type of spherulite forms. It should be noted that while the electrical conductivity at room temperature is $\sigma_{ac} = 6.4 \times 10^{-14}\,(\Omega \cdot m)^{-1}$, at the end of the reverse cooling process it has the value $\sigma_{ac} = 1.6 \times 10^{-13}\,(\Omega \cdot m)^{-1}$, i.e., σ_{ac} increases approximately 2.5 times.

Keywords: high-density polyethylene, gamma radiation, dose, heating–cooling cycle, temperature, electrical conductivity.

1. Introduction

Polymers and polymer-based composite materials play a leading role in the development of global industry. Polymer and polymer composite materials (PCMs) have not only been successfully applied in various industrial fields but have also become in high demand among consumers.

It should also be noted that the development of modern technologies is characterized by the need for new polymer composite materials that can be used in the development of solid-state electronic components. The acquisition and application of such materials is also attractive in terms of reducing the size of electronic devices and enabling the transition to molecular-level technologies that allow for the targeted transfer of electrical charges and energy. In recent years, the creation of materials containing micro- and nanoparticles of metal oxides has become widespread in the development of new polymer-based composite materials with unique and practically significant electrophysical properties [1–8].

The rapid development of modern atomic, space, and electronic industries requires the advancement of polymer materials used in these fields to meet contemporary standards. Newly developed polymer composite materials must exhibit high operational quality and be resistant to the effects of ionizing radiation. As a result of ionizing radiation, structural changes occur in polymers and the composite materials derived from them. Structural changes that occur after exposure to ionizing radiation lead to alterations in virtually all physical and chemical properties.

One of the current challenges is studying the changes that occur in polymers and composite materials derived from them after exposure to ionizing radiation. Therefore, studying the structure, physicochemical, electrophysical, and other properties of each polymer is one of the most important topics from both scientific and practical perspectives [4, 6–12].

In this study, we investigated the temperature dependence of electrical conductivity during the heating–cooling process of a pure high-density polyethylene (HDPE) sample modified by gamma radiation.

2. Experimental Methods

To obtain a pure polymer sample, powdered high-density polyethylene (HDPE) (brand 20806-024, average molecular weight 95,000, degree of crystallinity 52%, melting temperature T = 130 °C, density $\rho = 0.93$ g/cm³, volume resistivity $\rho_v = 1 \times 10^{16}$ Ω·cm) was used. HDPE powder is pressed into a metal mold with a thickness of 200 μm and a diameter of 40 mm using a hydraulic press at a pressure of 15 MPa and a temperature of 423 K for 5 minutes. The sample is then cooled to 273 K (in a water-ice mixture) to obtain pure polymer samples with a thickness of 170 μm and a diameter of 40 mm. A pure HDPE sample was exposed to γ-irradiation at an absorbed dose rate of 3.3×10^3 Gy/h using an MPX-γ-25M device with a ^{60}Co radiation source at room temperature (T = 293 K). The radiation doses (D) were 100, 200, and 500 kGy.

The temperature dependence of the electrical conductivity of the HDPE sample, both before (initial) and after irradiation, during the heating–cooling process was measured using an E7-20 immittance measuring device under alternating current (U = 1 V, ν = 1 kHz).

3. Experimental Results and Discussion

Figure 1 shows the temperature dependence of the alternating current electrical conductivity of the initial HDPE sample before irradiation during the heating–cooling process.

As shown in Figure 1, two temperature regions are observed in the temperature dependence of HDPE conductivity during both heating and cooling. In the heating process, the temperature ranges are 293–343 K (region I) and 343–403 K (region II). In the reverse process, the temperature ranges are 403–358 K (region I) and 358–293 K (region II). In the reverse process, the conductivity reaches a minimum at 358 K, curves 1 and 2 intersect at 333 K, and a hysteresis loop is formed. It should also be noted that at room temperature, the conductivity was $\sigma = 6.4 \times 10^{-14}$ $(\Omega \cdot m)^{-1}$, and during the reverse cooling process, at the end of the cycle, it increased by approximately 2.5 times to a value of $\sigma = 1.6 \times 10^{-13}$ $(\Omega \cdot m)^{-1}$.

It should also be noted that pure polymers contain significant contamination from catalyst residues, which also act as ion sources due to dissociation products. On the other hand, the mechanism of electrical conductivity in polymers also depends on their chemical structure and the charge carriers injected from the electrode [13].

Given that crystallizing polymers consist of both crystalline and amorphous phases, it should also be noted that the change in conductivity with temperature (during both heating and cooling) may be related to the mobility and relaxation processes of molecules [14].

Figure 2 (a, b, c) shows the temperature dependence of the electrical conductivity of a pure HDPE sample under heating–cooling conditions at doses of D = 100 kGy (a), D = 200 kGy (b), and D = 500 kGy (c).

As shown in Figure 2a, in pure HDPE at a γ-irradiation dose of D = 100 kGy, an increase in electrical conductivity is observed as a function of temperature. Before irradiation (D = 0), the conductivity at room temperature during the heating process was $\sigma = 6.4 \times 10^{-14}$ $(\Omega \cdot m)^{-1}$, while at D = 100 kGy, it increased to $\sigma = 4.2 \times 10^{-13}$ $(\Omega \cdot m)^{-1}$, representing an increase of approximately

6.6 times. In the cooling process at T = 293 K, the initial sample had a conductivity of $\sigma = 1.6 \times 10^{-13}$ $(\Omega \cdot m)^{-1}$, while at D = 100 kGy, the conductivity was $\sigma = 1.7 \times 10^{-13}$ $(\Omega \cdot m)^{-1}$. As shown in Figure 2, after γ-irradiation, the conductivity reaches a maximum at T = 353 K, $\sigma = 2.8 \times 10^{-10}$ $(\Omega \cdot m)^{-1}$. It should also be noted that in both heating and cooling processes, the conductivity values nearly coincide in the temperature range of 378–403 K, and a hysteresis loop forms at 378 K.

During the cooling process, a monotonic decrease in conductivity is observed up to T = 353 K, followed by a sharp drop down to T = 323 K. In the range of 323–293 K, σ_s remains practically constant. An amorphous–crystalline structure is formed in both unirradiated (initial) and irradiated polyethylene (PE) up to a dose of 55 kGy [9]. It should also be noted that in crystallizing polymers, irradiation leads to the breakdown of crystallites, resulting in a decrease in the overall degree of crystallinity of the polymer. Changes in conductivity with increasing radiation dose may be attributed to radiolysis products that remain in the material for extended periods, causing both a decrease and an increase in conductivity [15, 16].

Figure 2b shows the dependence of $\lg\sigma = f(T)$ under heating–cooling conditions for pure HDPE at a radiation dose of D = 200 kGy.

As shown in Figure 2b, the conductivity behavior at an irradiation dose of D = 200 kGy is nearly identical to that observed at D = 100 kGy. In the heating process, a conductivity of $\sigma = 4.3 \times 10^{-13}$ $(\Omega \cdot m)^{-1}$ was obtained at T = 293 K, while in the reverse process, $\sigma = 2 \times 10^{-14}$ $(\Omega \cdot m)^{-1}$ was observed, representing a one-order decrease. At a significantly higher radiation dose (D = 500 kGy, Fig. 2c), the conductivity increases and reaches a maximum at 373 K ($\sigma_{ac} = 1.43 \times 10^{-10}$ $\Omega \cdot m^{-1}$). Starting from 373 K, the conductivity decreases sharply and remains stable until the end of the temperature range. During the reverse cooling process, the conductivity decreases monotonically, reaching a minimum at 353 K, and then stabilizes at 293 K.

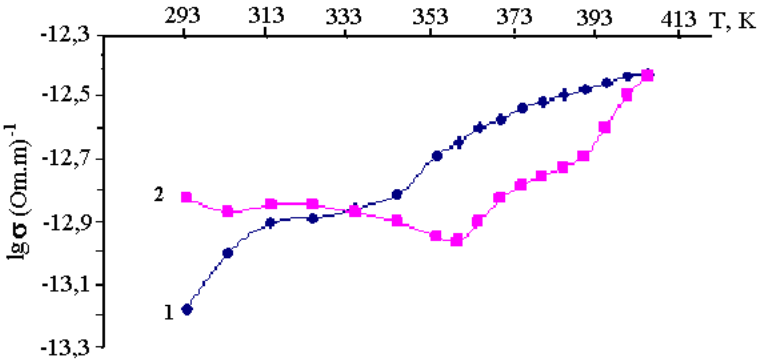
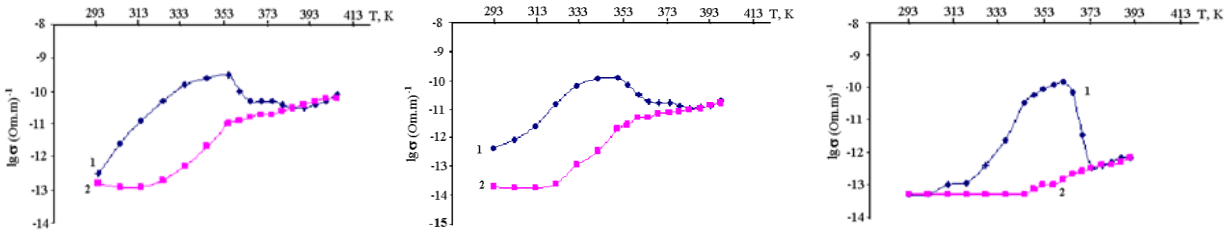


Fig. 1. Temperature dependence of the electrical conductivity of a pure HDPE sample before irradiation during the heating-cooling process: lg σ = f(T); 1 – heating, 2 – cooling.



a) b) c)

Fig. 2. Temperature dependence lg σ = f(T) of the electrical conductivity of a pure HDPE sample under alternating current during the heating-cooling process at absorption doses of γ-radiation: D = 100 kGy (a), D = 200 kGy (b), and D = 500 kGy (c). 1 – heating, 2 – cooling.

It should also be noted that comparing the $\log \sigma = f(T)$ dependence of conductivity before and after irradiation once again showed that the conductivity behavior during the heating-cooling process at radiation doses of 100–200 kGy is nearly identical. Thus, the decrease in conductivity is more pronounced in the polymer softening temperature range (333–353 K) during both the heating and cooling processes. This decrease may be associated with the weakening of bonds between polymer macromolecules as a result of the absorbed dose of γ-radiation. As seen in Fig. 2c, the temperature dependence of conductivity at a radiation dose of D = 500 kGy differs slightly from that observed at doses of 100–200 kGy. Thus, during the heating process, a sharp increase in conductivity was observed in the temperature range of 333–373 K, followed by a sharp decrease in the range of 373–393 K (Fig. 2c, curve 1). The increase in conductivity in the indicated temperature range may be attributed to excess charges and enhanced molecular mobility resulting from the absorbed dose of radiation [5, 8, 13, 14, 16]. During the reverse cooling process, the supramolecular structure of the polymer phase undergoes a significant change as a new type of spherulite forms.

It should also be noted that spherulites are commonly occurring molecular structures in crystalline polymers. Spherulites are polycrystalline structures with symmetry around the crystal center, formed by the aggregation of similarly oriented lamellae [6, 7, 10–12, 17].

4. Result

The electrical conductivity of the (initial) high-density polyethylene (HDPE) sample during the heating-cooling process before γ-irradiation is influenced by the mobility of charge carriers (ions) as well as by charge carriers injected from the electrode. The increase in conductivity due to irradiation is attributed to the formation of additional charge carriers in the sample, while the decrease results from the weakening of bonds between polymer macromolecules. As a result of irradiation, it was also observed that during the reverse cooling process, the supramolecular structure of the polymer phase undergoes a significant change, with the formation of a new type of spherulites.

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ТЕМПЕРАТУРНЫЕ ЗАВИСИМОСТИ ЭЛЕКТРОПРОВОДНОСТИ ПОЛИЭТИЛЕНА ВЫСОКОЙ ПЛОТНОСТИ, МОДИФИЦИРОВАННОГО ГАММА-ЛУЧАМИ В ПРОЦЕССЕ НАГРЕВА-ОХЛАЖДЕНИЯ

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Резюме: были исследованы температурные зависимости электрической проводимости при переменном токе (σ_{ac}) образца полиэтилена высокой плотности (ПЭВП), модифицированного гамма-лучами $\sigma_{ac} = f(T)$, в процессе нагрева-охлаждения. Электрическая проводимость в процессе нагрева-охлаждения чистого образца ПЭВП перед облучением (первичный) обусловлена подвижностью носителей заряда (ионов), а также носителей заряда, инжектированных из электрода. Увеличение проводимости в результате поглощающей дозы облучения связано с дополнительными носителями заряда, образующимися в образце, а уменьшение-с ослаблением связи между макромолекулами полимера в результате поглощающей дозы. В процессе обратного охлаждения образца ПЭВП после облучения надмолекулярная структура полимерной фазы претерпевает резкие изменения, так что здесь образуются сферолиты нового типа. Следует отметить, что в то время как электропроводность при комнатной температуре составляет $\sigma_{ac} = 6.4 \times 10^{-14}\,(\Omega \cdot м)^{-1}$, в конце процесса обратного охлаждения она получила значение $\sigma_{ac} = 1.6 \times 10^{-13}\,(\Omega \cdot м)^{-1}$, что означает, что σ_{ac} увеличивается примерно в 2,5 раза.

Ключевые слова: полиэтилен высокой плотности, гамма-излучение, доза, нагрев-охлаждение, температура, электропроводность.

QAMMA ŞÜALARLA MODİFİKASİYA OLUNMUŞ YÜKSƏK SIXLIQLI POLİETİLENİN QIZMA-SOYUMA PROSESİNDƏ ELEKTRİK KEÇİRİCİLİYİNİN TEMPERATUR ASILILIQLARI

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Xülasə: Qamma şüalarla modifikasiya olunmuş yüksək sıxlıqlı polimer (YSPE) nümunəsinin qızma-soyuma prosesində elektrik keçiriciliyinin dəyişən cərəyanda (σ_{ac}) temperatur asılılıqları $\sigma_{ac} = f(T)$ tədqiq edilmişdir. Şüalanmadan əvvəl (ilkin) təmiz YSPE nümunəsinin qızma-soyuma prosesində elektrik keçiriciliyi yükdaşıyıcıların (ion) yürüklüyü və həm də elektroddan injeksiya olunmuş yükdaşıyıcılarla bağlıdır. Şüalanmanın udulma dozası nəticəsində keçiriciliyin böyüməsi nümunədə yaranan əlavə yükdaşıyıclarla, azalması isə udulma dozası nəticəsində polimer makromolekulları arasında rabitəninn zəif olması ilə əlaqədardır. YSPE nümunəsinin şüalanmadan sonra əks soyuma prosesində polimer fazanın üstmolekulyar quruluşu kəskin dəyişikliyə uğrayır, belə ki, burada yeni tip sferolitlər əmələ gəlir. Qeyd etmək lazımdır ki, otaq temperaturunda elektrik keçiriciliyi $\sigma_{ac} = 6.4 \times 10^{-14}\,(\Omega \cdot \mathrm{m})^{-1}$ olduğu halda, əks soyuma prosesinin sonunda $\sigma_{ac} = 1.6 \times 10^{-13}\,(\Omega \cdot \mathrm{m})^{-1}$ qiymətini almışdır, yəni σ_{ac} təqribən 2,5 dəfə böyüyür.

Açar sözlər: yüksək sıxlıqlı polietilen, qamma şüalanma, doza, qızma-soyuma, temperatur, elektrik keçiriciliyi.