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RESEARCH ARTICLE

Features of the change in the thermal coefficient of electrical resistance upon heating electrically conductive composites of crystallizable polyolefins with carbon black

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Abstract

Objectives. To investigate electrically conductive polymer composite materials (EPCMs) based on crystallizable polyolefins and electrically conductive carbon black for the production of self-regulating heaters; to study the mechanism of the occurrence of positive and negative temperature coefficients (PTC and NTC) upon heating such composites.

Methods. A comprehensive study of the structure and properties of crystallizable EPCMs with electrically conductive technical carbon was carried out. In order to measure the electrical characteristics of the composites, they were compacted into plates to model polymer heaters. Contact electrodes made of an ungreased brass mesh were embedded in their ends. The temperature dependencies of the electrical characteristics of the samples were investigated in a modified thermal chamber of an FWV 633.10 Vicat softening temperature meter. The change in the degree of crystallinity was analyzed by means of differential scanning calorimetry with a NETZSCH DSC 204 F1 Phoenix calorimeter. The dilatometric and rheological characteristics of the samples were studied using an IIRT-AM melt flow index tester.

Results. It was determined that the self-regulation ability (an abnormally high positive thermal coefficient of electrical resistance) of self-regulating heaters made of composites of crystallizable polyolefins with electrically conductive technical carbon cannot be explained by the thermal expansion of EPCMs alone. It was shown that in crystallizable polyolefin-based EPCMs, the inversion of the thermal coefficients of electrical resistance (transition from PTC to NTC) is associated with a change in the aggregate state of EPCMs and the beginning of its transition to a viscous-flow state. A mechanism involving a sharp increase in the electrical resistance of self-regulating crystallizable polyolefin-based composite with electrically conductive technical carbon was proposed and substantiated. This mechanism takes into account the additional shear deformation effect produced on the crystalline phase of the EPCM by numerous expanding melt microvolumes formed at the early stages of the melting process with a minimum change in the degree of crystallinity.

Keywords

electrically conductive polymer composites, self-regulating heaters, polyolefins, electrically conductive carbon black, positive temperature coefficient of electrical resistance (PTC), negative temperature coefficient of electrical resistance (NTC)

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НАУЧНАЯ СТАТЬЯ

Особенности изменения термического коэффициента электрического сопротивления при нагревании электропроводящих композиций кристаллизующихся полиолефинов с техническим углеродом

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Аннотация

Цели. Исследовать электропроводящие полимерные композиционные материалы (ЭПКМ) на основе кристаллизующихся полиолефинов и электропроводного технического углерода (ЭТУ) для производства саморегулирующихся нагревателей. Изучить механизм возникновения эффектов положительного и отрицательного температурных коэффициентов (ПТК и ОТК) в процессе нагревания композитов.

Методы. Проведено комплексное исследование структуры и свойств кристаллизующихся ЭПКМ с ЭТУ. Для исследования электрических характеристик композиций были отпрессованы пластины с запрессованными на концах контактными электродами из обезжиренной латунной сетки, моделирующие полимерные нагреватели. Исследование зависимостей электрических характеристик образцов от температуры проводили в модифицированной термокамере прибора FWV 633.10 для определения температуры размягчения Вика. Изменение степени кристалличности исследовали методом дифференциальной сканирующей калориметрии на приборе NETZSCH DSC 204F1 Phoenix. Исследование дилатометрических и реологических характеристик образцов проводили на приборе для определения показателя текучести (ИИРТ-АМ).

Результаты. Установлено, что появление у саморегулирующихся нагревателей, изготовленных из кристаллизующихся полиолефиновых композиций с ЭТУ, способности саморегулирования (появления аномально высокого положительного термического коэффициента электрического сопротивления) нельзя объяснить только термическим расширением ЭПКМ. Показано, что в кристаллизующихся полиолефиновых ЭПКМ инверсия термических коэффициентов электрического сопротивления (переход от ПТК к ОТК) связана с изменением агрегатного состояния ЭПКМ и началом его перехода в вязкотекучее состояние. Предложен и обоснован механизм резкого роста электрического сопротивления саморегулирующихся кристаллизующихся полиолефиновых композиций с ЭТУ, учитывающий дополнительное сдвиговое деформационное воздействие на кристаллическую фазу ЭПКМ множества расширяющихся микрообъемов расплава, возникающих на ранних стадиях процесса плавления при минимальном изменении степени кристалличности.

Ключевые слова

электропроводящие полимерные композиты, саморегулирующиеся нагреватели, полиолефины, электропроводный технический углерод, положительный температурный коэффициент электрического сопротивления (ПТК), отрицательный температурный коэффициент электрического сопротивления (ОТК)

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INTRODUCTION

Electrically conductive polymer composite materials (EPCMs) with electrically conductive carbon black (ECB) as a conductive filler have found the following applications: in electrically conductive coatings; electromagnetic shielding for protection against static electricity; fuses against overloads in electrical grid equipment; temperature and pressure sensors [1–7]; and self-regulating heaters [8–12]. The production of self-regulating heaters is important for the safety of household heating appliances. The self-regulation of power of heaters based on EPCMs is due to an abnormally high positive temperature coefficient of electrical resistance (PTC) of crystallizable polymer matrices (e.g., polyolefins) in the temperature range of the onset of their melting [8–13]. This phenomenon is virtually absent in amorphous EPCMs.

An important condition for obtaining EPCMs with high electrical conductivity is believed to be the uniform distribution of ECB particles in the composite [14, 15]. Increased electrical resistance upon heating of self-regulating EPCMs is usually attributed to an increase in the distance between the particles and aggregates of ECB during thermal expansion upon heating [16–19]. However, studies indicate an increase in the electrical conductivity of materials with a nonuniform distribution of ECB in the crystallizable polymer phase, as well as in mixtures of such polymers [20–24]. This nonuniformity of such EPCMs makes the system of conductive channels formed from ECB particles less stable at high temperatures. This instability of EPCMs can lead to reversible disruptions of the conductive channels in the microzones between the melting crystalline formations [6, 10, 11, 13, 24]. With an increase in temperature, the number of such zones increases. The electrical resistance of the heater increases rapidly, and its power drops sharply. The purpose of the work was to confirm the mechanism of the occurrence of abnormally high PTC in polyolefin-based EPCMs.

EXPERIMENTAL

The objects of this study were thermoplastic polyolefins with different melting temperatures: stabilized cable high-density polyethylene (HDPE) 277-73 (GOST 16338-85[1]); low-density polyethylene (LDPE) 10813-020 (GOST 16337-77[2]); and polypropylene (PP) 01050 (TU 2211-074-05766563-2015[3]). The electrically conductive filler was UM-76 finely divided ECB (TU 38-10001-94) intended for use in EPCMs.

Composites were prepared using a VK-6 laboratory-scale two-roll mixing mill (*GRANAT*, Russia) with electric heating of the rolls at a mixing temperature of 180 ± 10°C. The UM-76 powder was added to a preliminarily prepared polyethylene melt. After homogenization, rolling was continued for 10 min. The ECB content in all the composites was the same and amounted to 20 wt % (11.7 vol %). It was previously shown that this UM-76 content is optimal for self-regulating EPCMs [9].

In order to study the electrical characteristics of the composites, samples were compacted from them at a pressure of 15.0 MPa at 180°C and cooled in a mold to 50°C. The samples consisted of plates with a length of $L = 120 \pm 5$ mm, a width of $b = 10 \pm 0.5$ mm, and a thickness of $\delta = 1.0 \pm 0.05$ mm. Contact electrodes made of an L-80 ungreased brass mesh (GOST 6613-86[4]) were embedded in their ends. Slow cooling guaranteed the stability of the structure of the properties of the samples. The electrical resistance of the samples was measured with a DT9208A ohmmeter (*DELTA Battery*, China). Tests at elevated temperatures were performed in a modified thermal chamber of an FWV 633.10 Vicat softening temperature (GOST 15088-2014[5]) meter (*Zwick Roell*, Germany) at a heating rate of ~3°C/min. The temperature coefficient of electrical resistance (TCR, α; K^{-1}) was calculated by the formula:

$$\alpha = \frac{\Delta\rho}{\rho_0 \Delta T}, \tag{1}$$

wherein $\Delta\rho$ is the change in the volume electrical resistivity at a temperature change ΔT (°C), and ρ_0 is the volume electrical resistivity ($\Omega\cdot$m) under normal conditions.

The change in the degree of crystallinity was studied by differential scanning calorimetry (DSC) with a DSC 204 F1 Phoenix instrument (*NETZSCH*, Germany) at a heating rate of 3°C/min. The degree of crystallinity α_{cr} was calculated by the formula:

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[1] GOST 16338-85. Interstate Standard. Low-pressure polyethylene. Specifications. Moscow: Standartinform; 2005.

[2] GOST 16337-77. Interstate Standard. High-pressure polyethylene. Specifications. Moscow: Standartinform; 2005.

[3] TU 2211-074-05766563-2015. Balene (polypropylene and propylene copolymers). Specifications. https://polimermsk.ru/image/catalog/product/passport/TU%202211-074-05766563-2015.pdf. Accessed May 22, 2024.

[4] GOST 6613-86. Interstate Standard. Square meshed woven wire cloths. Specifications. Moscow: Standartinform; 2006.

[5] GOST 15088-2014 (ISO 306:2004). Interstate Standard. Plastics. Method for determination of Vicat softening temperature of thermoplastics. Moscow: Standartinform; 2014.

$$\alpha_{cr} = \frac{\Delta H_{melt}}{\Delta H_{cr}}, \quad (2)$$

wherein ΔH_{melt} is the enthalpy of melting of the crystalline phase of the sample calculated taking into account the weight fraction of ECB (kJ/mol). ΔH_{cr} is the enthalpy of melting of the crystalline phase of the polymer (kJ/mol).

Dilatometric and rheological studies of the composites were made using an IIRT-AM melt flow index device (*Altavir*, Russia) (GOST 11645-2021[6]) and known methods described earlier [23]. Dilatometric tests were carried out by measuring the change in the height of cylindrical samples (with an accuracy of ±0.01 mm) in the working chamber of the IIRT-AM device. The coefficient of volumetric thermal expansion β (K^{-1}) was calculated by the formula:

$$\beta = \frac{\Delta v}{v_0 \Delta T}, \quad (3)$$

wherein Δv (cm^3) is the product of the displacement of the rod and the cross-sectional area of the cylindrical working chamber of the device at a change in the temperature in it of ΔT (°C), and v_0 is the volume (cm^3) of the pellet under normal conditions.

RESULTS AND DISCUSSION

The phenomenon of a sharp increase in electrical resistance with increasing temperature is an integral property of polymer self-regulating heating elements. This phenomenon is especially pronounced in crystallizable polyolefins. The dependencies obtained earlier [25] (Fig. 1) confirm this and have a shape characteristic of self-regulating composites with ECB.

All polyolefins presented in Fig. 1 are characterized by extreme changes in ρ/ρ_0 with increasing temperature. The highest value of ρ/ρ_0 upon heating is exhibited by the EPCM based on HDPE which has a degree of crystallinity α_{cr} of 70.8% at normal temperature. For PP and LDPE, the degrees of crystallinity are significantly lower: 48.1 and 41.1%, respectively.

Based on the results of our studies, the TCR α values (K^{-1}) of these EPCMs were calculated over a wide range of temperatures (Fig. 2). As can be seen from Fig. 2, the temperatures of minima of TCR virtually coincide with the temperatures of maxima of ρ/ρ_0 in Fig. 1.

Several temperature regions can be distinguished on the curves of these dependencies. They differ in magnitude and sign of the change in electrical resistance. At low temperatures, the resistance increases proportionally to the increase in temperature. Such a change is due to the volumetric thermal expansion of the EPCM and is characterized by the size of the temperature zone of TCR. The α values (K^{-1}) in this zone were as follows: LDPE, 0.0033; HDPE, 0.0014; and PP, 0.0024. As the temperature approaches the temperature regions of polymer melting, the increase in resistance accelerates exponentially (the so-called temperature zone of abnormal PTC). In Fig. 2b, for polyethylenes, the beginning of this zone approximately corresponds to a temperature of 60–70°C (for HDPE, this can be better seen in an enlarged figure); also for polypropylene, to 110–120°C. The power of self-regulating EPCMs is regulated at the beginning of the PTC zone. This is due to the intensification of the destruction of conductive channels of ECB in them. A further increase in temperature in the polymer melting region leads to an inversion of the electrical resistance change at its point of maximum and the occurrence of the phenomenon of NTC. The NTC temperature zone ends with the complete melting of the polymer and the transition of the EPCM to the temperature zone of volumetric thermal expansion of the melt. The change in electrical resistance in this zone is proportional to the change in temperature, and is characterized by the value of the melt TCR zone. It follows that the temperature zones of interest, PTC and NTC, are associated with different stages of the melting of the polymer matrix of the EPCM. Gradual melting causes a sharp (extreme) change in electrical

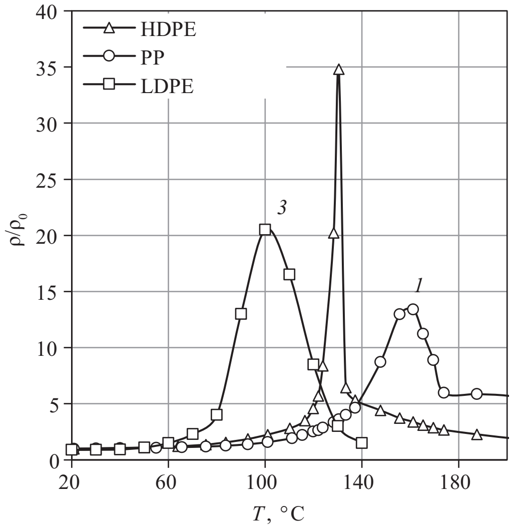

Fig. 1. Effect of temperature T (°C) on the normalized volume electrical resistivity ρ/ρ_0 (Ω·m/Ω·m) of polyolefin composites with ECB:
(*1*) polypropylene (PP), (*2*) high-density polyethylene (HDPE), and (*3*) low-density polyethylene (LDPE)

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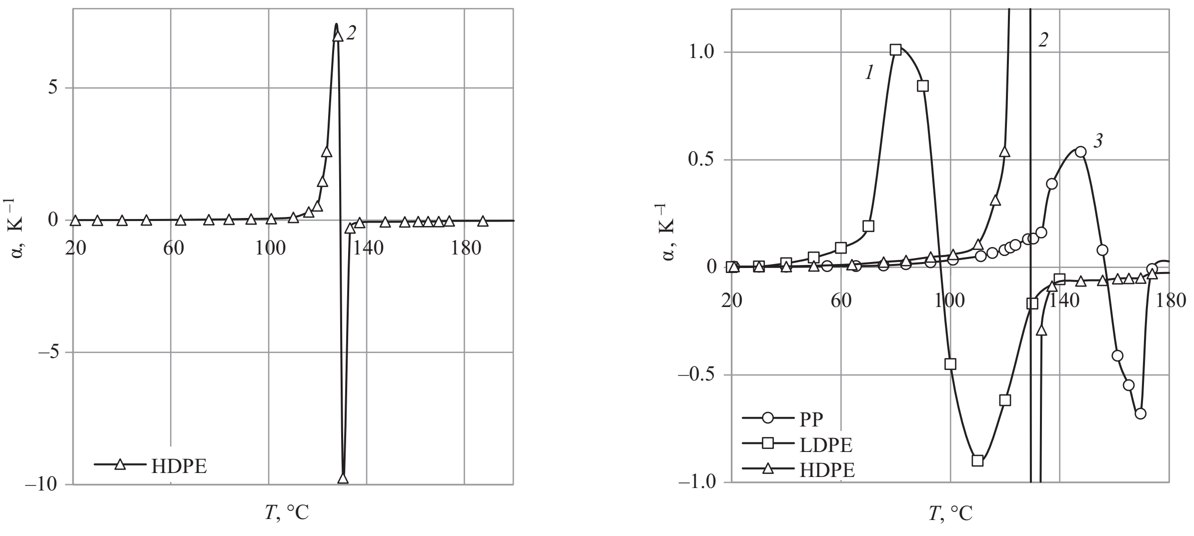
[6] GOST 11645-2021. Interstate Standard. Plastics. Methods for determination of flow index of thermoplastics melt. Moscow: Russian Institute of Standardization; 2021.



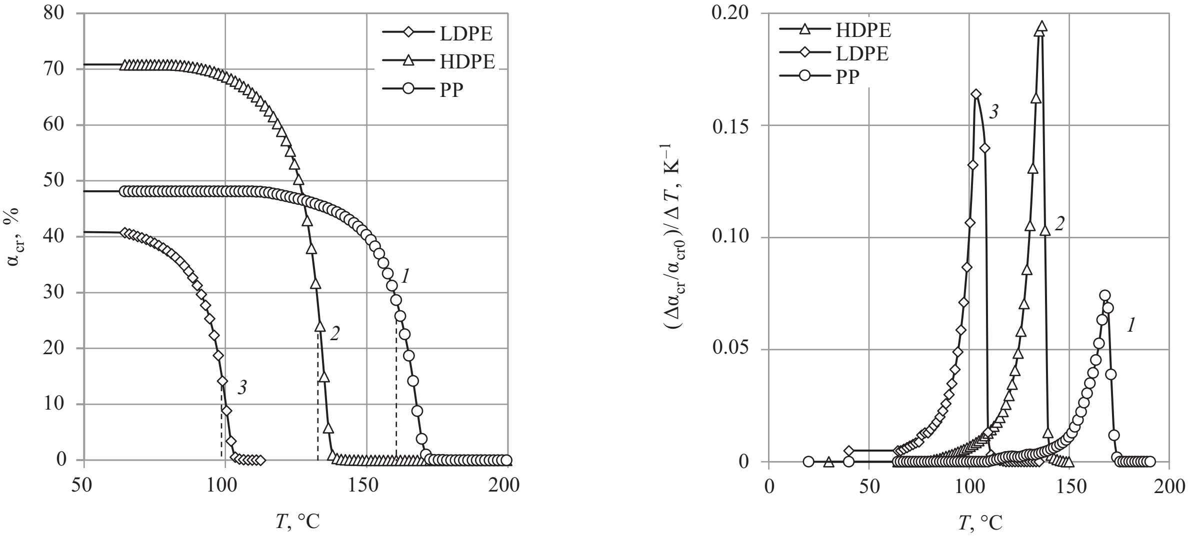
(a) (b)

Fig. 2. Effect of temperature T (°C) on the thermal coefficients of electrical resistance α (K^{-1}) of polyolefin composites with ECB: (*1*) PP, (*2*) HDPE, and (*3*) LDPE

resistance. It is important to note that, only in the TCR temperature zones of the melt, can the volumetric thermal expansion be considered the main mechanism of the effect of temperature on the electrical resistance of the EPCM. When transitioning from the PTC temperature zone to the NTC zone, the polymer continues to expand gradually, since the melting of the polyolefin matrix continues, while the fraction of the denser crystalline phase continues to decrease. This is confirmed by the dilatometry and DSC results given below.

In order to refine the mechanism of the occurrence of PTC and NTC, the effect of temperature was studied on the degree of crystallinity of the given EPCMs during melting. Figure 3 presents the results of these studies. The degrees of crystallinity α_{cr} of EPCMs were estimated at temperatures corresponding to the maximum values of ρ/ρ_0, at which inversion transitions from PTC to NTC were observed. For this purpose, the thermal coefficients of change in α_{cr} (Fig. 3b) were calculated, similar to thermal coefficients α and β.

Unlike electrical coefficients α, these coefficients are positive at all the temperatures studied. The temperatures of the maximum values of ρ/ρ_0 and the temperatures of the maxima of the thermal coefficients of change in α_{cr} in Fig. 3b were found to virtually coincide. In Fig. 3a, their positions are indicated by vertical dashed lines.



(a) (b)

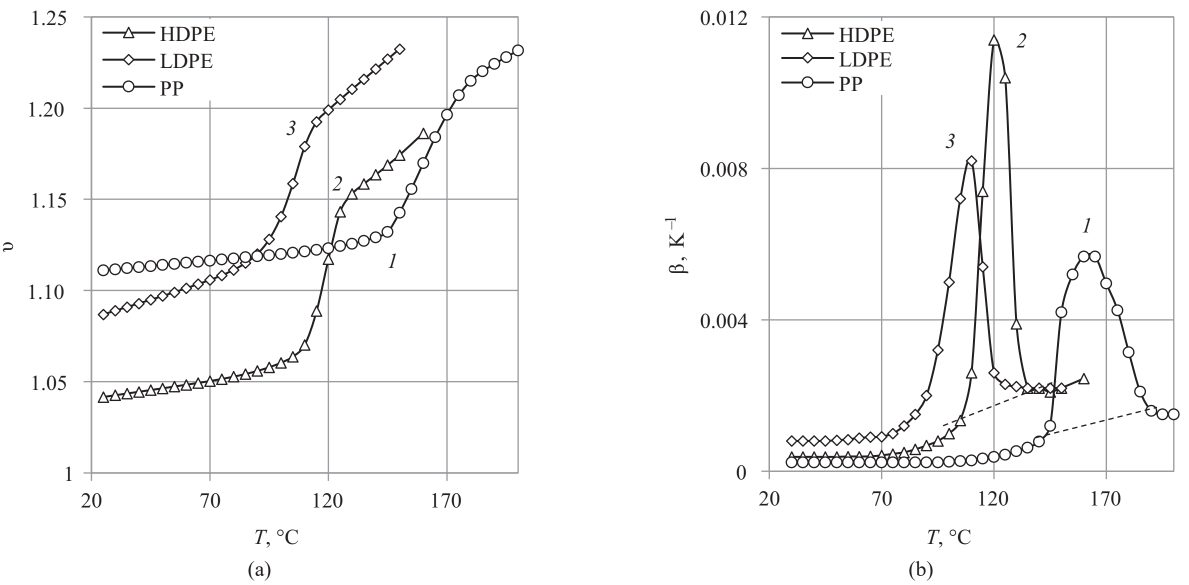
Fig. 3. Effect of temperature T (°C) on (a) the degree of crystallinity α_{cr} (%) and (b) the thermal coefficients of change in α_{cr} (K^{-1}) of polyolefin composites with ECB: (*1*) PP, (*2*) HDPE, and (*3*) LDPE

In crystallizable polyolefin-based EPCMs, the inversion of the change in the thermal coefficients of electrical resistance (the transition from PTC to NTC) occurs when the degree of crystallinity reaches 20–25%. Therefore, at degrees of crystallinity less than 20%, the barrier resistance may not appear, as in the case of amorphous polymers. In addition, this allows us to assume that the transition from PTC to NTC is caused by a sharp change in the aggregate state of the EPCM, and the beginning of its transition to a viscous-flow state. This is a result of fragmentation of the crystalline phase formed at the early stage of the crystallization process at high temperatures. The melt becomes a continuous phase. On the other hand, in the PTC temperature zone, the EPCM continues to contain the continuous crystalline phase with discrete inclusions of the melt formed from low-melting components of the crystalline phase formed at low temperatures at the late stage of the crystallization process at the boundaries of spherulites. Even a small decrease in the degree of crystallinity in the initial PTC temperature zone (at the temperatures of power regulation of the self-regulating heater) leads to significant destruction of conductive channels in ECB and a multiple increase in the resistance of the EPCM. This is due to the fact that self-regulating EPCMs respond with an increase in electrical resistance not only to thermal, but also to deformation effect [8, 9, 26, 27]. Therefore, the cause of the significant increase in resistance at these temperatures can also be the formation of melt microinclusions in the crystalline polymer and the increase in their volume. In this case, the shear deformation effect of many such expanding microvolumes is transferred to the crystalline phase. This causes additional shear destruction of conductive channels of ECB in the crystalline phase and accelerated increase in the electrical resistance of the EPCM in the PTC temperature zone even at a minimum change in the degree of crystallinity.

This factor ceases to act in the NTC temperature zone (in the continuous phase of the melt), despite the continued volumetric thermal expansion of the EPCM. Such a PTC mechanism confirms the weak manifestation of the phenomenon of PTC in EPCMs based on amorphous polymers [25] and its occurrence in mixtures of amorphous and crystallizable polymers [10, 22]. This can also explain the stabilization of the phenomenon of PTC and the absence of the phenomenon of NTC in self-regulating EPCMs subjected to radiation crosslinking [28–32] or chemical crosslinking [8–11, 33], thus deprived of the possibility of transition to a viscous-flow state.

In order to confirm the proposed mechanism, dilatometric tests of the given EPCMs were carried out. Figure 4a shows the dependencies of the change in their specific volume $\upsilon = V/V_0$ on temperature during thermal expansion of the EPCM. Here V_0 and V_T are the initial value of the sample volume and its current value at temperature T, respectively.

Naturally, the volume of all EPCMs increases in all the temperature zones described above. In the curves in Fig. 4a, the PTC and NTC temperature zones form a common melting zone, characterized by an accelerated smooth increase in the volume of the samples and is separated by two zones with a slow increase in the TCR. In this case, the calculated coefficient of volumetric thermal expansion in Fig. 4b is positive throughout the studied



(a) (b)

Fig. 4. Effect of temperature T (°C) on the specific volume υ during thermal expansion and (b) the coefficient of volumetric thermal expansion β (K^{-1}) of polyolefin-based composites with ECB: (*1*) PP, (*2*) HDPE, and (*3*) LDPE

temperature range. The temperature zones of the TCR of the melt are a continuation of the TCR zones of solid EPCMs (Fig. 4b, dashed lines). The temperatures of the maximum values of ρ/ρ_0 in Fig. 1 and the temperatures of the maxima in Fig. 4b are very close. However, the coefficients of volumetric thermal expansion β are greater than an order of magnitude lower than the thermal coefficients of electrical resistance α. This also indicates that volumetric expansion is not the only mechanism of the abnormally high PTC of EPCMs (Table 1).

Table 1. Initial thermal coefficients of electrical resistance α and the coefficients of volumetric thermal expansion β of polyolefin-based electrically conductive polymer composite materials (EPCMs)

Polyolefin	LDPE	HDPE	PP
α_0, K^{-1}	0.0033	0.0014	0.0024
β_0, K^{-1}	0.000195	0.00038	0.00011

In order to refine the features and mechanism of the change in the electrical resistance of the studied EPCMs during heating, it is useful to establish the activation energies of destruction of conductive channels formed by ECB particles using the Arrhenius equation [34]. In order to do this, an electrical characteristic needs to be selected. The behavior of this characteristic needs to be symbatic to that of this destruction. Change in electrical resistance is not suitable for this purpose, since it increases with a decrease in the number of conductive channels. However, if electrical resistance is replaced by electrical conductivity ($\sigma/\sigma_0 = \rho_0/\rho$), this problem can be resolved. The electrical conductivity should decrease proportionally to the decrease in these channels. Curve *1* in Fig. 5 illustrates the dependence of the logarithm of the electrical conductivity of the EPCM based on HDPE on the inverse temperature in the Arrhenius coordinates $\ln(\sigma/\sigma_0) = f(1/T, \text{K}^{-1})$.

The activation energies of the processes are proportional to the slopes of the experimentally obtained curves: $\ln(\sigma/\sigma_0) = f(1/T, \text{K}^{-1})$. The activation energy can change in different sections of the curves when the mechanism of the destruction of conductive channels in ECB changes.

The temperature dependence of electrical conductivity (Fig. 5, curve *1*) has several regions with different slopes. These are temperature zones with different activation energies: a low-temperature zone of TCR of solid EKPMs with the lowest slope and a PTC zone with the increasing slope. The NTC temperature zone, which was not used in the calculations, is represented by one point.

The low slope of curve *1* (low values of the activation energy E_{el} of change in electrical conductivity) in the TCR zone indicates that the mechanism of the decrease in the conductivity at these temperatures is the thermal motion of molecules, causing volumetric thermal expansion of the material. The increase in the slope at temperatures above 60°C (the increase in E_{el}) confirms the assumption about a change in the mechanism of the destruction of conductive channels in EKPM at the beginning of the PTC temperature zone. In the NTC zone, the electrical conductivity begins to increase.

For comparison, Fig. 5 also shows the DSC (curve *2*) and dilatometry (curve *3*) results processed in a similar manner. The decrease in the degree of crystallinity (curve *2*), related to the destruction of spherulites upon heating, should lead to the destruction of conductive channels in the EPCM. However, the shape of curve *2* differs significantly from the shape of curve *1*, analyzed above. The degree of crystallinity changes little until 110°C is reached. Curve *2* has virtually no temperature zone corresponding to the PTC zone on curve *1*, and the corresponding activation energy cannot be calculated.

The results of the dilatometric tests are shown in curve *3* of Fig. 5. By analogy with the dependence of σ/σ_0 on $1/T$ (K^{-1}), the inverse of the specific volume υ, the specific density $q/q_0 = 1/\upsilon$, was chosen as a dilatometric characteristic symbatic to σ/σ_0. The low values of the activation energy (the low slope of the line) indicate that the volumetric thermal expansion of the material is not the main cause of the occurrence of the abnormally high PTC of the studied EPCMs.

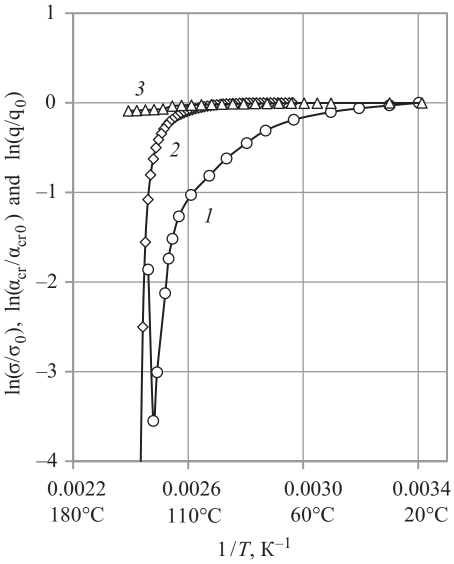


Fig. 5. Comparison of the temperature dependencies of the normalized values of electrical conductivity σ/σ_0, degree of crystallinity α_{cr}/α_{cr0}, and density q/q_0 of HDPE-based composites with ECB: (*1*) $\ln(\sigma/\sigma_0)$, (*2*) $\ln(\alpha_{cr}/\alpha_{cr0})$, and (*3*) $\ln(q/q_0)$

Figure 6 presents the temperature dependencies of σ/σ_0 on $1/T$ (K^{-1}) for all the studied polyolefin-based EPCMs. The dashed lines in Fig. 6 are tangents to the experimentally obtained curves in the regions of interest at the beginning of the PTC temperature zones. These are responsible for regulating the power of the EPCM heaters with increasing temperature.

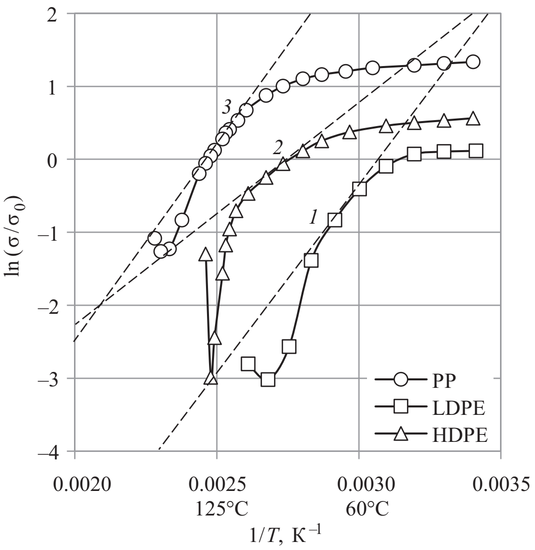


Fig. 6. Effect of temperature ($1/T$, K^{-1}) on the logarithms of the normalized values of electrical conductivity σ/σ_0 of polyolefin-based composites with ECB: (*1*) PP, (*2*) HDPE, and (*3*) LDPE

Table 2 presents the results of the calculation of the activation energies E_{el} of these processes occurring in these temperature zones of change in electrical conductivity. Table 2 also shows the values of the activation energies E_{vf} of viscous flow of melts, as determined by rheological studies.

Table 2. Calculated activation energies E_{el} and E_{vf} of destruction of conductive channels in the PTC zone and viscous flow of melts of polyolefin-based EPCMs

Polyolefin	LDPE	HDPE	PP
E_{el}, kJ/mol	41.6	29.3	45.1
E_{vf}, kJ/mol	45.5	30.5	45.4

The closeness of the E_{el} and E_{vf} values can be considered as confirmation of the expected influence of shear effect on the crystalline phase of numerous expanding microinclusions of the melt formed at the early stages of melting of polyolefin-based EPCMs.

CONCLUSIONS

A comprehensive study of the structure and properties of crystallizable polyolefin-based EPCMs with ECB was made. It was determined that the self-regulation ability (an abnormally high positive thermal coefficient of electrical resistance) of self-regulating heaters made of composites of crystallizable polyolefins with ECB cannot be explained by the thermal expansion of EPCMs alone. It was shown that in crystallizable polyolefin-based EPCMs, the inversion of the thermal coefficients of electrical resistance (transition from PTC to NTC) is due to a change in the aggregate state of EPCM and the beginning of its transition to a viscous-flow state.

A mechanism of the sharp increase in the electrical resistance of self-regulating crystallizable polyolefin-based composites with ECB was proposed and substantiated. This mechanism takes into account the additional shear deformation effect on the crystalline phase of the EPCM of numerous expanding melt microvolumes formed at the early stages of the melting process with a minimal change in the degree of crystallinity.

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Authors' contributions

A.V. Markov—creation of the concept of the study, processing the experimental data.

A.E. Zverev—conducting the experimental studies, processing the experimental data.

V.A. Markov—adjustment of the concept of the study.

The authors declare no conflicts of interest.

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