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RESEARCH ARTICLE

Effect of relaxation processes during deformation on electrical resistivity of carbon black polypropylene composites

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Abstract

Objectives. *To study the relationship between bending deformation and the change in the electrical resistance of carbon black polypropylene composites.*
Methods. *Conductive polypropylene composites filled with carbon black UM-76 were investigated. The samples were deformed and kept under constant bending at temperatures of 20–155°C.*
Results. *The deformation of the samples led to a reversible increase in their electrical resistance, while subsequent holding of the samples in the deformed state was accompanied by an exponential drop in their electrical resistance. The average times and activation energies of the electrical relaxation of the deformed polypropylene composites were calculated (30–32 kJ/mol) and compared with similar characteristics of polyethylene composites (15–16 kJ/mol).*
Conclusions. *The electrical resistance relaxation of deformed carbon black polypropylene composites at elevated temperatures is similar to their stress relaxation. The average times and activation energies of the electrical relaxation of deformed polypropylene composites are comparable with similar data on their mechanical relaxation. It was found that these electrical and mechanical phenomena are based on the same underlying physical processes.*

Keywords: *conductive polypropylene composites, carbon black, electrical resistivity, deformation, relaxation, PTC effect*

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НАУЧНАЯ СТАТЬЯ

Влияние релаксационных процессов при деформировании на электрическое сопротивление полипропиленовых композитов с техническим углеродом

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Аннотация

Цели. *Работа посвящена изучению влияния деформации изгиба при повышенных температурах на изменение электрического сопротивления электропроводящих полипропиленовых композитов, наполненных техническим углеродом.*
Методы. *Исследовались полипропиленовые композиты с техническим углеродом УМ-76. Образцы изгибались и выдерживались при заданном прогибе в интервале 20–155 °C.*
Результаты. *При деформировании образцов наблюдался обратимый рост электрического сопротивления. Последующая выдержка образцов в деформированном состоянии сопровождалась экспоненциальным падением их электрического сопротивления. Были рассчитаны средние времена и энергия активации электрической релаксации деформированных полипропиленовых композитов (30–32 кДж/моль), а также проведено их сравнение с аналогичными характеристиками полиэтиленовых композитов (около 14–16 кДж/моль).*
Выводы. *При механическом деформировании электропроводящих полипропиленовых композитов с техническим углеродом, в том числе при повышенных температурах, характер релаксации электрического сопротивления аналогичен характеру релаксации механического напряжения. Средние времена и энергия активации электрической релаксации деформированных полипропиленовых композитов сопоставимы с аналогичными показателями для механической релаксации. Это указывает на общий механизм этих процессов.*
Ключевые слова: *электропроводящий полипропилен, технический углерод, электрическое сопротивление, деформация, релаксация, эффект ПТК*

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INTRODUCTION

Self-regulating heating cables, thermostatic heating elements, thermostatic devices, and self-disconnecting electrical fuses are made based on electrically conductive polymer composites containing carbon black (CB) [1]. The ability of these materials to change their electrical resistance during mechanical deformation [2] has opened up new possibilities for their use, e.g., as internal mechanical stress sensors and damage indicators [3]. Regardless of the shape and size of the electrically conductive fillers, the change in the electrical conductivity of the composites during macroscopic deformation is usually explained by the change in the distances between the conductive particles [4]. The change in electrical resistance during the deformation of electrically conductive composites is associated with the restructuring processes of the system of electrically conductive channels, i.e., the destruction of existing channels or the emergence of new channels [5, 6]. The prevalence of a particular process and, consequently, the increase or decrease in the electrical resistance depends on the nature of the polymer matrix and the content of the electrically conductive filler [7, 8]. The formation of electrically conductive channels during the deformation of a composite is also influenced by the orientation phenomena in the polymer matrix. This effect in particular manifests in the anisotropy of electrical properties during the stretching of an electrically conductive composite due to the appearance of anisotropy of the composite structure when deforming polymer macromolecules [7]. In the case of polymeric electrically conductive composites filled with CB, the mechanical and electrical characteristics change interdependently. This opens up the possibility of studying relaxation phenomena based on data on electrical conductivity changes in a material that cannot be studied with other methods [9]. During cyclic deformation, electrically conductive polymer composites show a hysteresis of electrical resistance similar to the hysteresis of mechanical stress [4]. The highest sensitivity of electrical resistance to temperature change (positive temperature coefficient [PTC]) and tensile deformation is observed when the content of the electrically conductive filler corresponds to the percolation threshold region [10–12]. It is with this content that the electrically conductive polymer composite material is suitable for use in thermostatic heating elements. Simultaneously, the presence of a negative temperature coefficient (NTC effect) is an undesirable effect because it can lead to failure of the polymer composite heater. This effect can be eliminated by radiation crosslinking or chemical crosslinking of the polymer matrix of an electrically conductive composite or by using an electrically conductive composite polymer matrix of a mixture of polyethylene (PE) with a more heat-resistant polymer, e.g., polypropylene (PP) [13, 14]. Note that the influence of various types of deformation, such as tension, compression, and shifting, on the electrical resistance of electrically conductive polymer composites is currently being studied in detail [6, 15, 16]. However, there is practically no data in the scientific and technical literature on the effect of bending deformation on electrical resistance. This phenomenon is especially important for self-regulating heating cables, as these composite materials are used in their manufacturing. This is the main deformation type for heating cables.

The purpose of this work is to study the relationship between deformation and the magnitude of the electrical resistance of PP composites with CB.

EXPERIMENTAL

We studied PP composites (PPG 1120-16 grade, *Stavrolen*, Budenovsk, Russia, TU 2211-008-50236110-2006) with an optimal content of conductive UM-76 CB for heating elements (*Omsk Carbon Group*, Omsk, Russia, TU 38-10001-94) at 20 wt % (11.7 vol %).

The compositions were prepared on a Brabender plastograph (*Brabender GmbH*, Duisburg, Germany) at 200°C, as in [17]. The samples were prepared by pressing at 200 ± 2°C, with the contact lamination made of L-80 brass mesh (GOST 6613-86[1]), as described in [17]. The electrical resistance of the samples was measured with a DT9208A ohmmeter.

The study of the effects of the bending deformation was carried out from 20 to 155°C in a SNOL 3.5 oven (*ThermIKS*, Russia), as described in [18]. In this case, the samples were deformed at a constant injector movement speed of 5 mm/s to a fixed depth of deflection to attain a deformation of 0.1 ± 0.01%. At larger deformations, the samples broke at temperatures below 100°C.

RESULTS AND DISCUSSION

The materials under study were characterized by a sharp increase in electrical resistance due to the rearrangement of the polymer crystal structure in the melting temperature range as well as the intense destruction of the conductive channels formed by the CB particles [17]. The temperature range in the region of the peak in the dependence of the electrical resistance

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[1] GOST 6613-86. Square meshed woven wire cloths. Specifications. Moscow: Standartinform, 2006.

on the test temperature practically coincided with the temperature range of PP melting. Figure 1 shows how the samples' temperature affected the change in the electrical resistance of the investigated PP composite.

The effect of the tripping "barrier" resistance (PTC) was also retained for the deformed samples. Figure 2 shows the kinetic dependences of the changes in the electrical resistance of the samples at different temperatures.

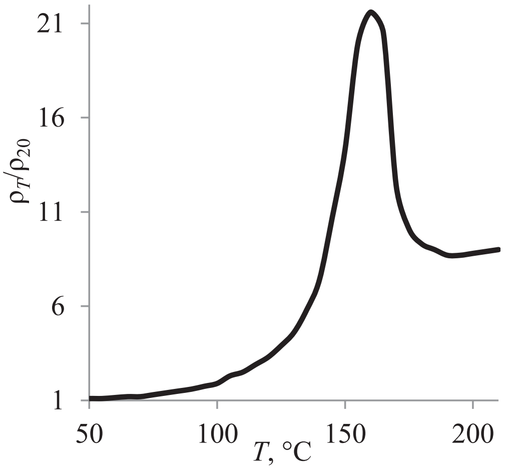

Fig. 1. Dependence of the relative electric volume resistance (ρ_T/ρ_{20}) of the polypropylene samples on temperature.

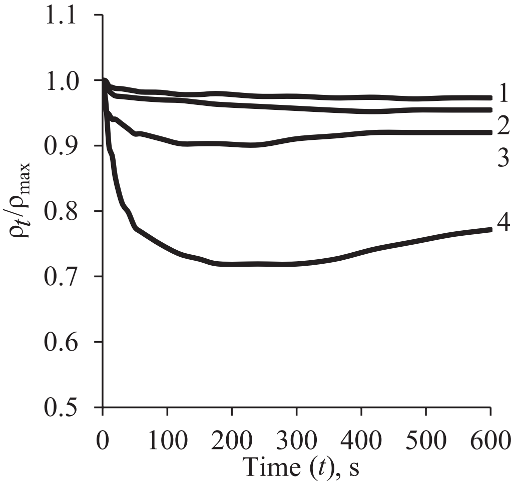

Fig. 2. Change in the relative (ρ_t/ρ_{max}) specific volume electric resistivity during and after bending (f = 0.11) at various temperatures: (1) 90°C, (2) 125°C, (3) 140°C, (4) 155°C.

The obtained time dependences of the changes in electrical resistivity were similar to the well-studied dependences of mechanical stress relaxation [19]. It can be seen in Fig. 2 that during the sample deformation, a jump of electrical resistance was observed from the value of electrical resistance (ρ_T; resistance of an undeformed sample at the test temperature) to the maximum value (ρ_{max}) corresponding to a given deformation (ρ_0 at heat treatment time t = 0). Furthermore, the electrical resistivity at all temperatures exponentially decreased within 4–5 min at a constant bending strain. At longer times (in Fig. 2, the relaxation times are limited to 10 min) and at 140°C and higher temperatures approaching the melting points of the PP matrix, the resistance began to increase (Fig. 2, curves 3 and 4).

It became apparent that the value of the maximum resistance at the same relative deformation at the moment of deformation (as in [20]) depended little on temperature up to 140°C because the effect of the deformation at low temperatures (in the forced highly elastic state of the polymer) on the deformed PP structure also depended little on the temperature. A noticeable increase was observed only at temperatures close to the PP melting point. This effect was similar to that of the increase in the electrical resistance of undeformed samples at the temperatures of the onset of polymer melting in Fig. 1 and was probably of the same nature [20]. As assumed in [20], the relaxational decrease in the electrical resistance at higher temperatures was associated with the restoration of the conductive channels formed by the CB particles. The higher the sample temperature, the greater this decrease in electrical resistance [20]. Isometric heat treatment of a deformed PP composite under isometric conditions also led to the restoration of the conductive channel system [20]. Once again, we could say that this relaxation phenomenon was similar to the NTC effect characterized by decrease in the height of the electrical resistance "barrier" peak upon heating non-deformed samples at high temperatures in Fig. 1. When deformed at higher temperatures (close to the PP melting point), the abovementioned destruction of the conductive channels formed by the CB particles occurred more intensively, possibly due to the recrystallization of the composite's PP matrix [17].

To study the mechanism of electrical resistance relaxation, we could use the concept of average relaxation time, as in the case of mechanical stress relaxation. We used Eq. (1) to calculate the relaxation times [9]:

$$\ln\frac{\rho_t-\rho_{\min}}{\rho_{\max}-\rho_{\min}}=\frac{t}{\tau} \qquad (1)$$

where ρ_t, ρ_{max}, and ρ_{min} are the current (at time point t), maximum (at the beginning of the relaxation process), and minimum (equilibrium) values, respectively, of the specific volumetric electrical resistance (Ohm·m) and τ is the average relaxation time (s). Using these relations, we could calculate the average times of electrical resistance relaxation at the studied temperatures[2]. The obtained relaxation times made it possible to calculate the activation energies of the electrical relaxation by analogy with the activation energy of mechanical relaxation [19]:

$$\ln\tau = \ln\tau_0 + \frac{U_{el}}{RT}, \qquad (2)$$

where τ is the average relaxation time (s) at temperature T (K), τ_o is a constant with the dimension of time (s), R is the universal gas constant equal to 8.31 J/(mol·K), and U_{el} is a coefficient independent of temperature (J/mol). The value of U depended on the average size of a kinetic unit (a molecule or part of a molecule) that participated in the thermal motion (relaxation process), as in the case of PE composites [18]. It is known [19] that the activation energy of viscous flow ($U_{vis.flow}$; the motion of segments upon melt shear) for PP and PE is 45–50 and 30–35 kJ/mol, respectively. Relaxation times (τ) linearly depend on the reciprocal of temperature (1/T, K) in a wide temperature range (see Fig. 3).

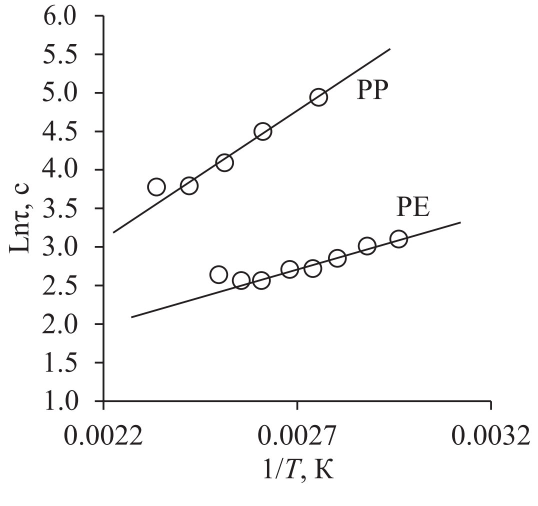

Fig. 3. Dependence of the relaxation time of the electrical resistance of polyethylene (PE) [20] and polypropylene (PP) on the test temperature.

The calculated values of the "electrical" activation energies of the studied processes (U) were U_{PP} = 30–32 kJ/mol and U_{PE} = 15–16 kJ/mol. Note that for PP, the value of the "mechanical" activation energy (U) decreased from $U_{vis.flow}$ ~45 kJ/mol in the viscous fluid state to $U_{high.elastic}$ ~32 kJ/mol at temperatures below the temperatures of the onset of PP melting upon its transition to the forced highly elastic state [19]. In linear high-density PE, a corresponding decrease occurred from $U_{vis.flow}$ ~30 kJ/mol to $U_{high.elastic}$ ~17 kJ/mol [18, 19]. In our case, the temperature coefficient (U_{el}) for the electrical relaxation of PP and, as shown earlier, high-density PE [20] in the solid state practically coincided with the above values. Our results indicated a direct relationship between electrical relaxation and mechanical relaxation due to the segmental mobility of the polymer macromolecules.

CONCLUSIONS

This study showed that during the mechanical deformation of electrically conductive PP composites with CB at elevated temperatures the nature of electrical resistance relaxation is similar to the nature of mechanical stress relaxation. The average times and activation energies for the electrical relaxation of deformed PP composites are comparable to those for mechanical relaxation, which indicates the general nature of these processes.

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Authors' contribution

A.V. Markov – design of the research concept, development of the experiment, discussion and analysis of the results, writing the text of the article;

K.S. Tarasova – studying the properties of samples, processing and analysis of the data obtained, discussion of the results;

V.A. Markov – studying the properties of samples, data collection and processing, discussion of the results, formatting the text of the article.

The authors declare no conflicts of interest.

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