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The influence of carbon black content on temperature dependences of electrical conductivity of polymer composite

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It was found that in the region of the percolation threshold, depending on the dominance of one or another conduction mechanism, the temperature dependence of the specific volume resistivity $\rho(T)$ of the polymer composite based on a matrix of ethylene vinyl acetate is significantly transformed. With an increase in the CB content, there is a decrease by several orders of magnitude in the maximum value of the relative resistivity $\rho(T)_{\max}/\rho_{20}$ in its temperature dependence. Peroxide crosslinking of matrix macromolecules leads to a change in the nature of the temperature dependence of resistivity.

Keywords: polymer composites, carbon black, electrical conductivity, temperature dependence.

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Electrically conductive polymer composites attract high interest of researchers and developers of new materials because of their wide application [1–3]. Regardless of the relatively high percolation threshold ($C \approx 15\%$), the usage of carbon black (CB) as a filler ensuring electrical conductivity does not complicate the procedure of mixing used to achieve the necessary homogeneity of composites and provides the required physical-mechanical and process characteristics in producing, e.g., screening braids of high-voltage cables. Due the carbon nanotubes' specific geometry and low content ($\sim 1.5-2\%$), their employment does not make unlikely occurring of local centers of discharge and breakdown at the places of the nanotube emergence to the surface of the composite conductive layer. Investigation of physical properties of composites filled with CB has been a subject of a great number of papers both in our country and abroad [2–8].

The purpose of this paper is studying the influence of the CB content on temperature dependences of conductivity of a polymer composite based on the ethylene vinyl acetate matrix. As a filler providing electrical conductivity, CB C40 of the „OMCARB"series was used whose content (C) in the polymer matrix varied from 15 to 35 mass percent. The composites were produced by blending in laboratory extruder EX30. After that a part of materials was held in molten dicumyl peroxide at the temperature of 55°C for 30 min. Samples in the form of plates 2 mm thick were fabricated by compression molding. To fix the temperature dependences of resistivity $\rho(T)$, rectangular samples 10×100 mm in size were put into furnace SNOL 58/350 where the temperature was varied with the step of 3–5°C and maintained accurately to ±1°C. The samples were kept at each measurement temperature for 5 min. Resistivity of the samples with resistivity $\rho \geqslant 10^6\,\Omega \cdot \mathrm{cm}$ was measured using device Megger MIT1025 according to the two-probe scheme; at lower ρ, resistivities were measured according to the four-probe scheme. Composites with various CB contents were also studied by differential scanning calorimetry (DSC) using the METTLER TOLEDO DSC 823e device.

Fig. 1 presents the dependences of resistivity at the temperature of 20°C (ρ_{20}) on the CB content for the samples saturated and non-saturated with peroxide. The results presented in this figure show that the percolation region is associated with the range of the composite CB concentration of $C \approx 10-25\%$ for the peroxide-nonsaturated samples and $C \approx 15-30\%$ for peroxide-saturated samples. The mechanism providing a sharp (especially in the percolation region) increase in ρ as a result of saturating with peroxide is described in [9]. Figs. 2, *a–e* present the direct and inverse (on decreasing temperature) temperature dependences of relative $\rho(T)/\rho_{20}$ for initial samples with different CB contents. The same figures present

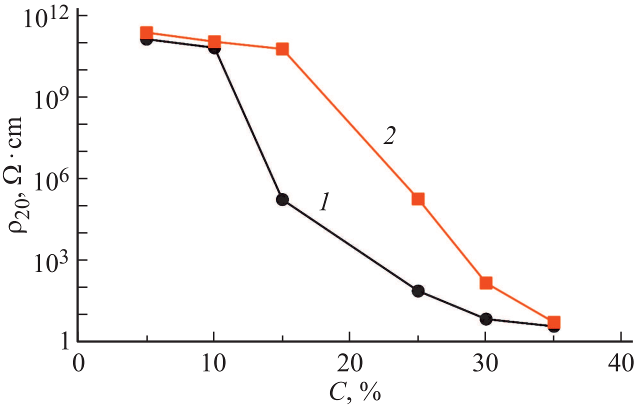

Figure 1. Plot of resistivity of composite vs. CB content at the temperature of 20°C. *1* — initial samples, *2* — samples saturated with peroxide.

direct and inverse DSC curves plotted taking into account the coefficient allowing for the C value. For clarity, they were corrected by the ordinate (multiplied by factor $k = 1/(1 - C)$). The presented DSC curves show that the positions of the main (dominating) and less-intense high-temperature peak which is caused by the presence of an extra polymer crystalline phase [10] are almost invariant. At the same time, temperature dependences $\rho(T)$ undergo essential transformation with increasing CB content. As Fig. 2, *a* shows, in the case of the sample with concentration $C = 15\%$ approximately corresponding to the percolation threshold, the maximum $\rho(T)_{\max}$ is observed in the straight line representing dependence $\rho(T)/\rho_{20}$ at the temperature significantly lower than the melting point of the main polymer crystalline phase ($T \approx 91^\circ$C corresponding to the peak in the DSC curve). The $\rho(T)_{\max} position$ ($T \approx 86^\circ$C) corresponds approximately to the beginning of this phase melting. At the melting point, a drastic drop of $\rho(T)/\rho_{20}$ is observed. In the inverse $\rho(T)$ dependence, the $\rho(T)_{\max}$ maximum is observed at the temperature corresponding to the termination of the crystallization process; the sharpest increase in $\rho(T)$ takes place at the crystallization point.

At such a CB concentration ($C = 15\%$), the conductive grid formation from the CB particles is not yet accomplished, and the main conduction mechanisms are the hopping mechanism consisting in hopping of electrons with energies being close to the Fermi level but exceeding the potential barrier, and mechanism caused by electron tunneling through the potential barriers between conductive CB particles located close to each other (at less than 5 nm) [11]. The actuality of such a conduction mechanism in the samples with CB concentration $C = 15\%$ is confirmed by that the current density j dependence on the field strength E (JV characteristic) is quite accurately describable by the Fowler–Nordheim relation [12]:

$$j = AE^2 e^{-\frac{B}{E}},$$

where A and B are constants. In the samples with $C = 25$, 30 and 35%, the $j(E)$ dependence was linear.

This is just the fact that causes specific features inherent to temperature dependence $\rho(T)$, namely, the fact that the hopping conduction mechanism and probability of the carriers tunneling are predominantly influenced by thermally stimulated processes occurring in the temperature range preceding the melting point of the composite polymer crystalline phase.

When C increases to 25% (Fig. 2, *b*), the maximum in the $\rho(T)$ dependence shifts towards higher temperatures. At such a concentration, the distance between the CB particles decreases, and the electric conductivity begins to be contributed by not only the mechanism caused by the current carriers tunneling but also by the mechanism caused by a grid of CB particles and their agglomerates directly contacting each other, namely, by the so-called ohmic conductivity.

If the CB content increases to 35% when, as ρ_{20} values for such a sample show, a denser conductive grid of CB particles is formed which just establishes the predominant conduction mechanism, the character of temperature dependence $\rho(T)$ changes (Fig. 2, *c*). One can see that at this concentration the fastest growth of $\rho(T)$ takes place at the temperature equal to the melting point of the polymer crystalline phase, which is caused by destruction of conductive bridges formed by the CB particles. The $\rho(T)$ maximum is observed already at $T \approx 98^\circ$C, i. e., not at the temperature of the beginning of the polymer crystalline phase melting as in the sample with $C = 15\%$ but at the temperature of the end of melting. The $\rho(T)$ decrease with further increase in T is caused by restoration of the conductive bridges due to agglomeration of the CB particles due to enhancement of their mobility. In the inverse dependences, the $\rho(T)$ maximum approximately corresponds to the temperature of the beginning of this phase crystallization. Fig. 2, *c* also shows that at concentration $C = 35\%$ the fraction of the second (higher-temperature) polymer crystalline phase initiated by the CB particles increases, and its influence on the $\rho(T)$ temperature dependence becomes more considerable [10]. Fig. 2 and the table show that a drastic reduction of relative variations in $\rho_{\max}/\rho_{20}$ with increasing C takes place. The temperature resistivity coefficient (TRC) also decreases sharply

$$\beta = \frac{1}{\rho_{20}} \frac{\partial\rho}{\partial T},$$

both the positive TRC (PTRC) and negative TRC (NTRC) determined at the bending points of the relevant sections of the $\rho(T)/\rho_{20}$ dependence being decreased. This decrease may be explained by that, as noticed above, the increase in C promotes formation of a denser conductive grid of CB particles and their agglomerates, and also by that the polymer matrix influence on the grid state variations weakens with decreasing matrix fraction. The table also demonstrates that NTRC of the sample with $C = 15\%$ is about 1.5 times higher than PTRC. In the samples with higher CB content, NTRC is, vice versa, lower (about twice) than PTRC. In addition, in the sample with $C = 15\%$ the $\rho(T)$ dependence has a sharper character. The peak width is approximately twice lower than in other samples.

It is also necessary to notice that the difference between the $\rho(T)$ dependence for the sample with $C = 15\%$ and similar dependences for samples with higher BC contents correlates with the value of the ρ_{20} variation occurring due to saturation with peroxide (Fig. 1). Just at this CB concentration, the maximal variation in ρ_{20} takes place.

Saturation of samples with peroxide and occurring crosslinking of the polymer matrix macromolecules lead, as noticed above, to an essential, especially in the percolation region, increase in ρ_{20} (see the table) and transformation of temperature dependence $\rho(T)$. The drastic increase in the resistivity of the sample with $C = 15\%$ has made impossible sufficiently accurate fixation of temperature dependence $\rho(T)$. Temperature dependences $\rho(T)/\rho_{20}$ for samples with $C = 25$ and 35% are presented in Figs. 3, *a*, *b*. The increase in C from 25 to 35% is followed by more an

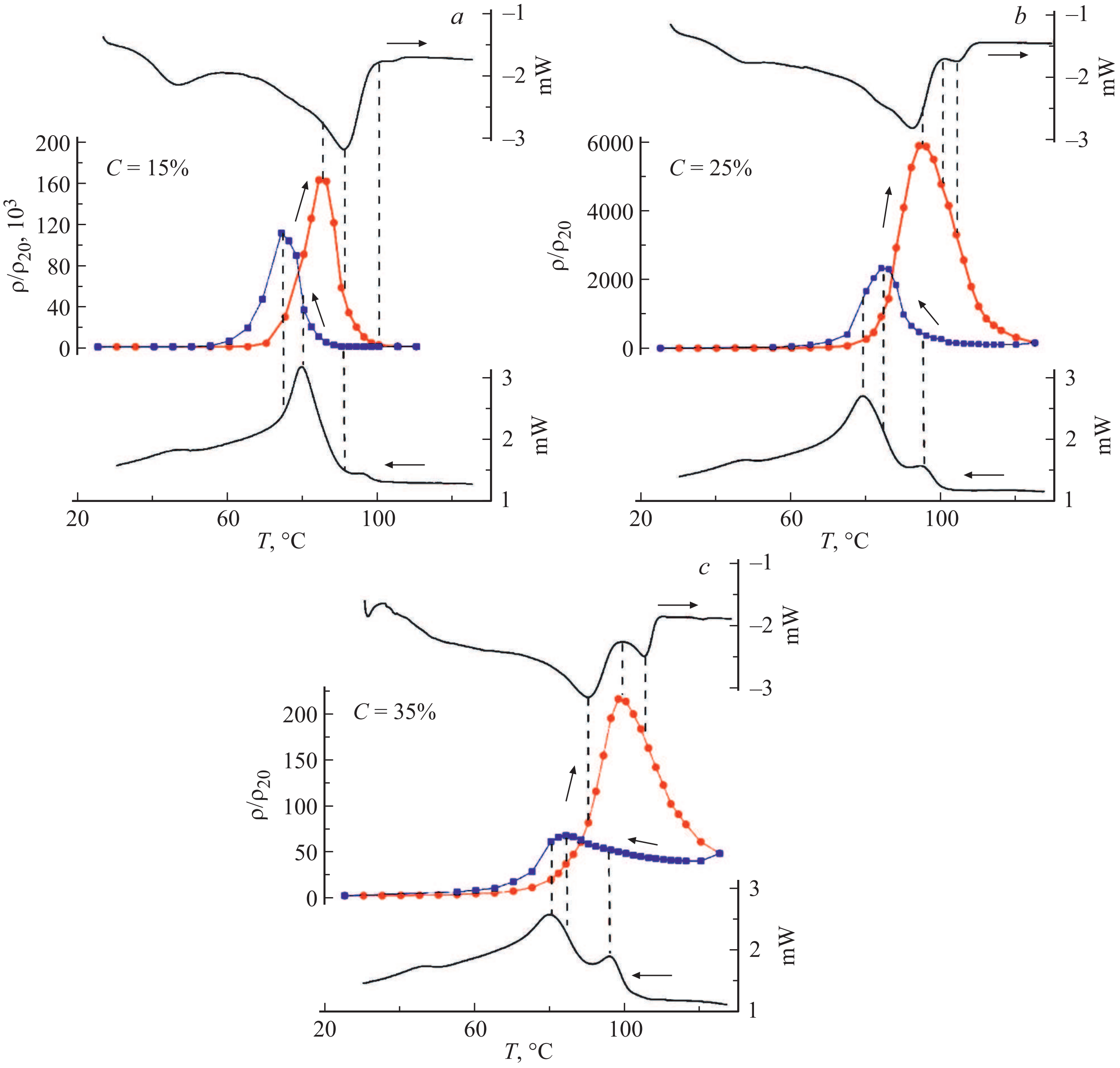

Figure 2. Direct and inverse temperature dependences of resistivity $\rho(T)/\rho_{20}$ of the initial composite with various CB contents. The relevant DSC curves are presented above and below.

Parameters of the composite samples

C,%	Initial samples				Samples saturated with peroxide		
	ρ_{20}, $\Omega \cdot$ cm	$\rho_{\max}/\rho_{20}$	PTRC	NTRC	ρ_{20}, $\Omega \cdot$ cm	$\rho_{\max}/\rho_{20}$	PTRC
15	159000	161006	21603	32787	$5.61 \cdot 10^{10}$	–	–
25	68.5	5902	853	435	$1.68 \cdot 10^{5}$	646	121
30	6.3	492	59	28	134	80.2	5.6
35	3.4	216	18	10.46	4.8	31.2	2.1

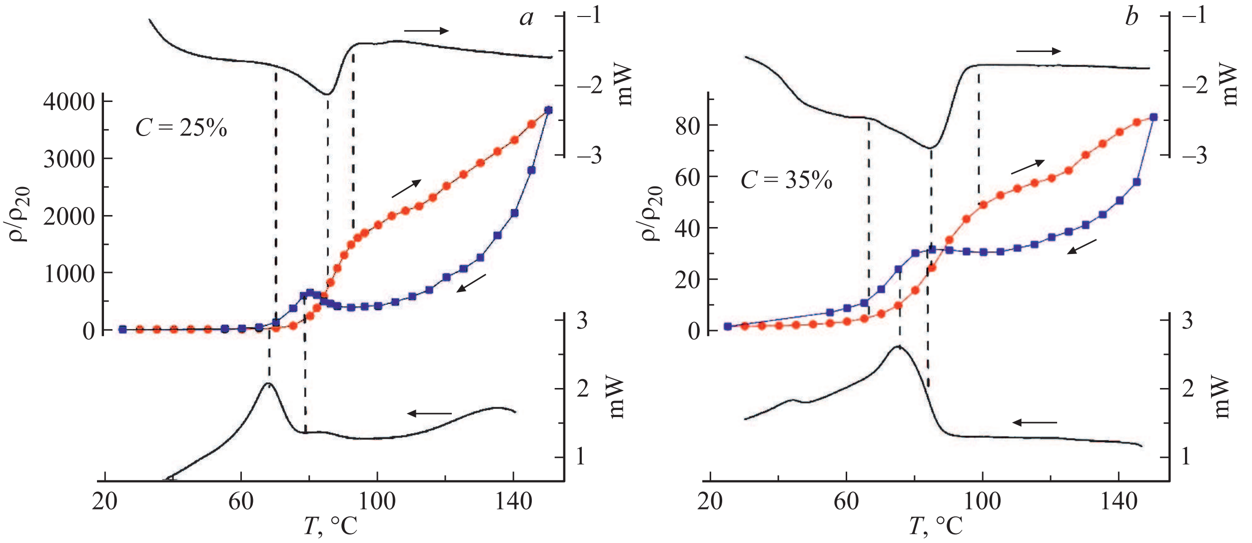

Figure 3. Direct and inverse temperature dependences of resistivity $\rho(T)/\rho_{20}$ of the peroxide-saturated composite with various CB contents. The relevant DSC curves are presented above and below.

order of magnitude decrease in both the $\rho(T)/\rho_{20}$ value corresponding to the local maximum and in TRC which changes its sign twice in the inverse dependence $\rho(T)$ and in the direct dependence in the second cycle and subsequent ones. As for the correlation between dependences $\rho(T)/\rho_{20}$ and DSC curves, the melting point of the polymer crystalline phase in crosslinked composites also corresponds to the section of the fastest $\rho(T)$ growth. The melting termination manifests itself as a break in the $\rho(T)/\rho_{20}$ curve.

Thus, the following conclusions can be made based on the results obtained in this study.

1. It was found that in the region of the percolation threshold, depending on the dominance of one or another conduction mechanism, the temperature dependence of the specific volume resistivity of the polymer composite based on the ethylene vinyl acetate matrix is significantly transformed. In the case of the hopping conduction mechanism and tunneling mechanism, the determining influence on the ρ variation value is exerted by thermally stimulated processes taking place at the temperatures preceding the melting point of the polymer crystalline phase. The ohmic conduction mechanism is affected mostly by the processes proceeding at the temperature corresponding to the end of this phase melting.

2. The increase in the CB content causes a decrease by several orders of magnitude not only in the specific volume resistivity ρ_{20} but also in the $\rho(T)_{\max}/\rho_{20}$ maximum in its temperature dependence. Therewith, the position of the $\rho(T)_{\max}$ maximum shifts towards higher temperatures.

3. Within the entire CB concentration range under study, the temperature hysteresis of $\rho(T)/\rho_{20}$ is observed which is most prominent in samples not saturated with peroxide. This is because of the difference in the characters of the processes of destruction and formation of conductive bridges during melting and crystallization of the polymer crystalline phase of the composite.

Conflict of interests

The authors declare that they have no conflict of interests.

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