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The influence of carbon black content on current-voltage characteristics of polymer composites

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The influence of the concentration (C) of technical carbon (CB) on the current-voltage characteristics (CVC) of composites based on an ethylene vinyl acetate matrix has been studied. It has been established that in polymer composites with low ($C = 5\%$) and high ($C \geqslant 25\%$) concentrations, the conductivity is practically independent of the electric field strength. In composites with CB concentrations corresponding to the percolation region, the presence of two pronounced segments of the CVC was found. After reaching a certain threshold field, a sharp increase in conductivity was observed. The behavior of the current-voltage characteristics of such composites in the region of high fields is described with good accuracy by the Fowler–Nordheim expression.

Keywords: polymer composites, electrical conductivity, carbon black, current-voltage characteristics

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Carbon-containing polymer composites attract a great deal of attention of researchers and engineers looking for novel materials [1–4]. It is known [5] that the mechanism of electric conduction in such materials has a complex nature specified both by the carbon filler type and by the composition and properties of the polymer matrix. Therefore, it is hard to calculate theoretically the dependence of electric conductivity of such composites (and the corresponding current-voltage characteristics) on the filler concentration [6,7].

The aim of the present study is to examine the influence of the carbon black (CB) content on the current-voltage characteristics (CVCs) of polymer composites with an ethylene vinyl acetate matrix. The filler providing electric conduction was carbon black C40 produced by „OMCARB“ Its content varied from 5 to 35% (mass percentage). Composites were produced by mixing with the polymer matrix in melt in an EX30 laboratory extruder. CVCs were measured at room temperature. A Megger MIT1025 tester was used to record CVCs in samples with CB concentration $C = 5$, 10, and 15%, which have high values of resistivity ρ. Rectangular voltage pulses produced with a high-voltage electronic switch were used to avoid heating of the samples with moderate ρ. Dependences $I(U)$ were measured with both gradually increasing (forward dependence) and decreasing (reverse dependence) voltages. In addition, the electric field was applied multiple times (in up to four cycles). Dependences of current density j on field strength E were calculated based on the measured U and I values.

Figures 1, *a–d* present dependences $j(E)$ for composites with a CB content of 5–35%. It is evident that CVCs underwent a significant transformation as the CB concentration in the composite increased. At a low CB concentration ($C = 5\%$), forward and reverse dependences $j(E)$ were linear in nature and matched almost perfectly within the entire studied E interval (Fig. 1, *a*). Dependence $j(E)$ remained unchanged when the field was applied for the second time. The current density was on the order of 10^{-5}–10^{-4} A/m^2. When the CB concentration increased to $C = 10\%$, which corresponds to the percolation region [8], dependence $j(E)$ assumed a fundamentally different nature (Fig. 1, *b*). It can be seen that $j(E)$ started increasing sharply as soon as a certain E threshold was crossed. The reverse $j(E)$ dependence differed somewhat from the forward one. When the electric field was applied for the second time, dependence $j(E)$ changed slightly, but CVCs became stabilized in the third and the fourth cycles, and forward and reverse dependences matched each other. The current density for these samples fell within the 10^{-3}–10^{-2} A/m^2 range. The transformation of dependence $j(E)$ with an increase and a subsequent reduction in E was the most pronounced in samples with $C = 15\%$ (Fig. 1, *c*). It is evident that current density j grew sharply following the initial enhancement of field strength E , reached its maximum, and then decreased noticeably, eventually attaining saturation. Reverse dependence $j(E)$ had a markedly different shape; consequently, hysteresis was observed. When $j(E)$ was measured for the second time, the current density increased less significantly and its maximum was less pronounced, although the forward dependence in this cycle was also positioned slightly above the reverse one. Forward and reverse dependences $j(E)$ matched almost completely in the third measurement cycle and remained unchanged in subsequent cycles (i.e., became stabilized). The conductivity increased sharply when the CB content reached $C = 25$ and 35%; consequently, the shape of the $j(E)$ dependence changed profoundly. It follows from Fig. 1, *d* that the CVCs for composites with $C = 25$

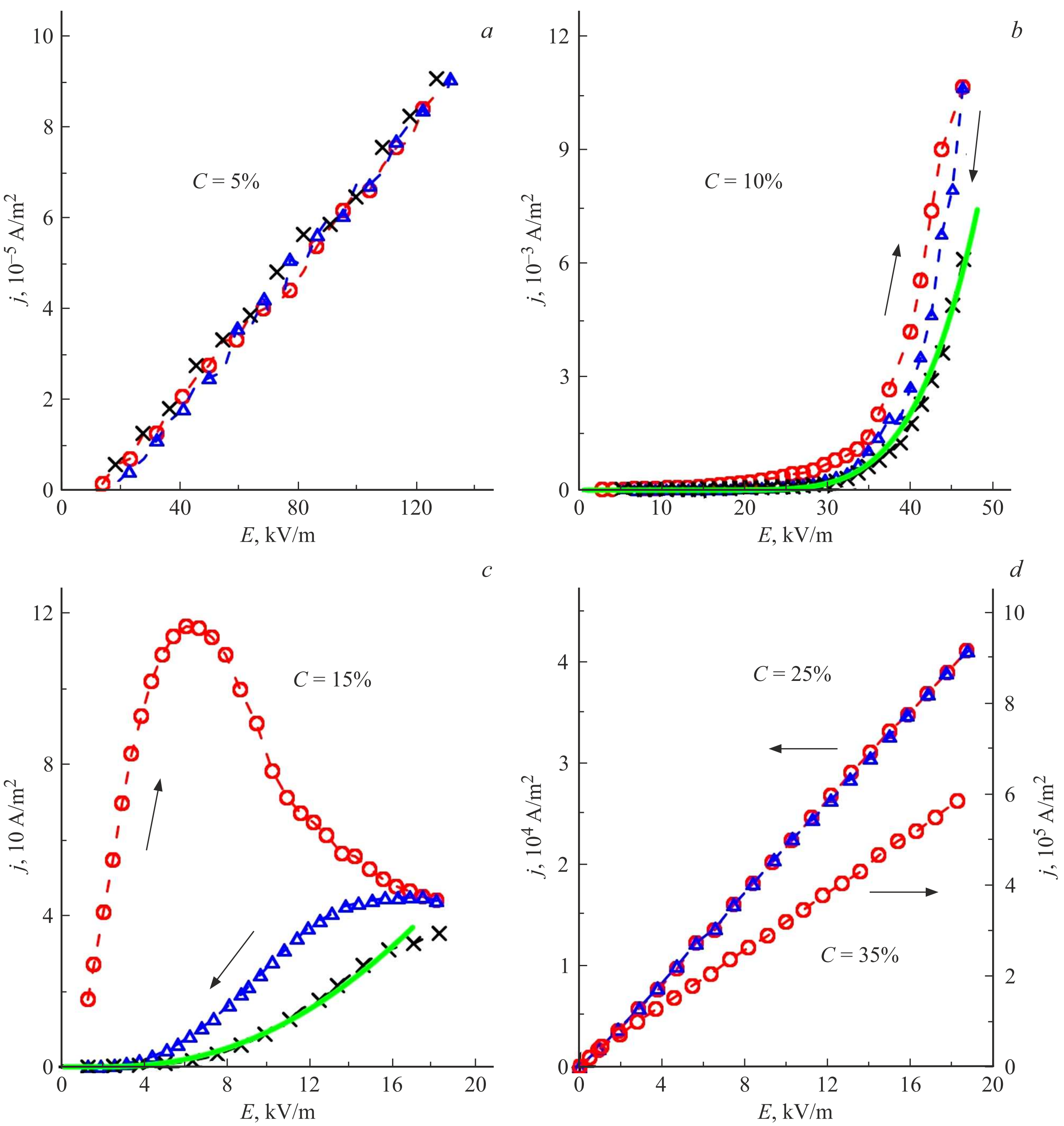

Figure 1. Experimental dependences $j(E)$ in composites with different CB content. Circles and triangles correspond to forward and reverse dependences, respectively, for the first cycle; crosses correspond to forward dependences for the third cycle; solid curves represent the calculated data.

and 35% were linear, and the current density was on the order of $\sim 10^4$ and 10^5 A/m^2, respectively. Note that the above-described behavior of dependences $j(E)$ at different C was reproduced in several batches of composite materials produced at separate times.

The observed marked CVC transformation induced by a change in the CB content of polymer composites may be attributed to the following. The distances between conducting centers (CB particles) present in a material at low concentrations are relatively long, and the conductivity of this composite is governed by the polymer matrix conductivity, which has a fairly complex nature with electronic and ionic contributions [1].

The well-pronounced nonlinearity of CVCs of composites with $C = 10\%$ (specifically, the sharp increase in conductivity with increasing electric field strength) is attributable to the fact that the interparticle distance at this CB concentration becomes sufficient for the mechanism controlled by field (autoelectronic) emission to produce a significant contribution to conductivity at certain E values. It follows from the Fowler–Nordheim model [9] for electric conduction induced by field emission that the dependence of current density j on E may be written as

$$j = A\frac{E^2}{\varphi}\exp\left(-\frac{B\varphi^{3/2}}{E}\right), \qquad (1)$$

where A and B are constants and φ is the electronic work function. Note that local electric field E_L acting between particles may be much stronger than applied field $E = U/L$, where L is the interelectrode distance. One may write E_L as $E_L = \beta E$, where β is the field intensification factor that depends both on the particle surface morphology and the interparticle distance and, consequently, increases with C.

The calculated $j(E)$ dependences are represented by solid curves in Figs. 1, b, c. it can be seen that experimental dependences $j(E)$ stabilized after the second field application cycle agree well with the calculated ones at the corresponding A and B values. Figure 2 shows experimental dependences $j(E)$ in Fowler–Nordheim coordinates $(\ln(j/E^2) = f(1/E))$. It is evident that the dependence for samples with $C = 10\%$ has two linear sections: a nearly horizontal one in the region of weaker fields and an inclined one in stronger fields. The horizontal section corresponds to quadratic dependence $j = kE^2$, while the inclined section follows expression (1) fairly accurately. Figures 1, b, c demonstrate that threshold field strength E, which corresponds to the onset of an exponential j rise, for the composite with $C = 15\%$ is significantly lower than the one for the composite with $C = 10\%$: approximately 3.8 and 38 kV/m, respectively. Notably, the transition from one section to another becomes more gradual when C increases to 15%.

An anode in the Fowler–Nordheim field emission model is exterior to the triangular near-cathode potential barrier that is shaped by the electric field and „rounded" by the field of a „mirror" image $U(z) = U_0 - eEz - e^2/4z$, where e is the electron charge and z is the distance from the surface. It is easy to demonstrate that the height and width of this barrier decrease with increasing E. Therefore, one might assume that the kink of the $\ln(j/E^2) = f(1/E)$ curve (Fig. 2) and the transition to an inclined linear section correspond to field strength E at which the width of the potential barrier at the Fermi energy level becomes equal to the distance between CB particles. As E increases further, the neighboring particle emerges from the potential barrier region and dependence $j(E)$ becomes aligned with the Fowler–Nordheim expression for field emission. Dependence $j(E)$ in weaker fields has a different nature. The lowering of the field threshold with increasing C may be attributed to the growth of field intensification factor β mentioned above.

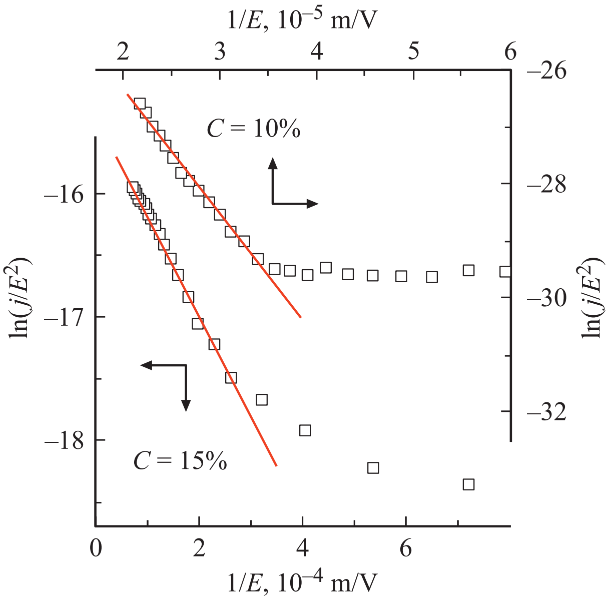

Figure 2. Experimental dependences $j(E)$ in Fowler–Nordheim coordinates for composites with CB content $C = 10$ and 15%.

The features of CVCs for the composite with $C = 15\%$ (specifically, the presence of a maximum in the initial $j(E)$ curve) are apparently attributable to an abrupt enhancement of the ionic conduction contribution due to the intensification of local fields. Residues of polymerization catalyst molecules, products of destruction and dissociation of polymer macromolecules, etc, may serve as sources of ions in a polymer matrix. At concentration $C = 15\%$, the field strength becomes sufficient for activation of the ionic conduction mechanism that is related to the distortion of profiles of ion potential wells. This conduction has $j \sim E$ within a wide range of E values [1]. Therefore, the linearity of the initial section of forward dependence $j(E)$ agrees with the assumption that the conduction mechanism is ionic. The peaking and subsequent decay of $j(E)$ may be attributed to the fact that the ionic composition becomes less rich (ions of different signs associate and recombine) as electric current flows through the composite. This explains why the hysteresis of dependence $j(E)$ is less pronounced in further (the second and subsequent) CVC measurement cycles and dependence $j(t)$ is decaying (Fig. 3) at a fixed E value corresponding to the maximum of $j(E)$. Note that the nature of dependence $j(E)$ remained unchanged when the polarity of the applied field was switched.

The Ohmic mechanism, which is driven by conducting chains of contacting CB particles and their agglomerates, produces the dominant contribution to conduction at concentrations $C = 25$ and 35%. The current density for these composites is 3-4 orders of magnitude higher than the one for the composite with $C = 15\%$. The contribution of the ionic mechanism, which produced the $j(E)$ maximum in the sample with $C = 15\%$, is lost almost completely against this background. Consequently, forward and reverse CVCs of composites with $C = 25\%$ are linear, match each other, and do not change when the electric field is applied repeatedly.

Thus, the following conclusions may be made.

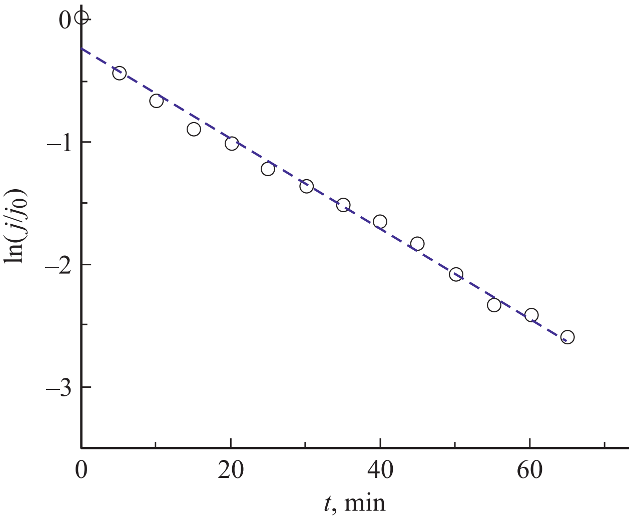

Figure 3. Dependence of j on time t for the sample with CB content $C = 15\%$.

1. The conductivity of composites with low ($C = 5\%$) and high ($C \geqslant 25\%$) CB concentrations is almost independent of the strength of the applied electric field. Forward and reverse CVCs match each other fairly accurately.

2. The CVCs of composites with a CB concentration of 10 and 15%, which corresponds to the percolation region, have two well-defined sections. The conductivity increases sharply when a certain field threshold, which gets lower as the CB content increases, is crossed. The nonlinear behavior of these CVCs is characterized fairly accurately by the Fowler−Nordheim expression.

3. The emergence of a maximum in the initial CVC, the hysteretic nature of the curve, and its well-marked transformation in composites with CB content $C = 15\%$ may be attributed to ionic conduction.

Conflict of interest

The authors declare that they have no conflict of interest.

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