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Effect of carbon black content on the effective permittivity of ethylene vinyl acetate matrix composites

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A sharp increase in the effective permittivity of composites with an ethylene vinyl acetate matrix at concentrations of carbon black corresponding to the percolation region was established, as well as the presence of a maximum of dielectric losses at a concentration when the dominant contribution to conductivity is due to field emission. A correlation was revealed between the dependences of the effective permittivity and conductivity on the content of carbon black. A contactless technique is presented that allows determining the permittivity of semiconducting materials using the capacitor method.

Keywords: polymer composites, effective permittivity, carbon black, electrical conductivity.

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Polymer composite materials filled with electrically conductive nanosized particles attract research attention and are of practical interest, since their electrophysical characteristics, such as conductivity and permittivity, may be adjusted within a wide range. The possibility of achieving the required values of these parameters is what drives the use of such materials as effective radiation-absorbing shells, antistatic coatings, etc. [1–5]. A fairly high permittivity coupled with a low level of dielectric losses makes these materials fit for use not only as conductive, but also as refractive materials for electric field equalization.

The dielectric properties of composites based on polymers and carbon fillers have been studied by many research groups. It was demonstrated that the real part of effective permittivity ε' increases with increasing carbon filler content [6–8]. For example, an increase in ε' with increasing concentration of carbon black in a composite with an ethylene propylene diene matrix was reported in [7]. This was attributed to the influence of interfacial polarization at the interface between the polymer matrix and filler particles. As was noted in [8], the Bruggeman approach to calculation of permittivity of a medium with conducting particles is more rigorous than the Maxwell–Garnett one.

The calculation of ε' becomes significantly more complicated in the case where conductive filler particles have a complex and varied shape and composites contains both individual particles and their agglomerates. These include polymer composites based on an ethylene vinyl acetate matrix filled with carbon black, which are of great practical importance (specifically, they are used to fabricate screens for high-voltage power cables). Therefore, the study of the influence of carbon black content on the electrophysical characteristics of the above composites is relevant.

The present study is focused on examining the dependence of the real part of effective permittivity ε' and loss tangent $\operatorname{tg}\delta$ of composites on carbon black content ν in an ethylene vinyl acetate matrix. The composites were prepared by mixing C40 carbon black with a particle size of 20–60 nm [9] into a matrix melt using an EX30 laboratory extruder. The carbon black content varied from 0 to 35 mass%. The capacitor (parallel plate) method was used to determine the permittivity. The measuring capacitor electrodes had the shape of a circle with a diameter of 25 mm and a thickness of 1.5 mm. The influence of edge effects on C was taken into account in accordance with the following expression [10]:

$$C = \varepsilon_0 \frac{\pi R^2}{d} + \varepsilon_0 R \left(\ln \frac{16\pi R}{d} - 1 \right) = C_0 + \Delta C,$$

where ε_0 is the permittivity of vacuum, R is the electrode radius, and d is the interelectrode distance.

The value of ΔC corresponding to the measuring cell used in the present study was 0.54 pF. The parasitic capacitance of the measuring cell and lead wires was 2.7 pF and was also taken into account in the determination of ε'. The pressure of electrodes on the sample was 1 N/cm^2. The samples for capacitance and $\operatorname{tg}\delta$ measurements were round disks with a diameter of 25 mm and a thickness of 1.5 mm. Megger MIT1025 and RIGOL DM3058 instruments were used to measure the bulk resistivity of high-resistance composites and low-resistance composites with carbon black content $\nu > 20\,\%$, respectively. The capacitance and the loss tangent at a frequency of 50 Hz were measured with a Vector 2M device, while an E4-7 instrument was used at 50 kHz.

It is hard to determine the permittivity of semiconducting materials, especially when reach-through conductivity is established in the sample and correct capacitance measurements become impossible. The following method of determination of ε' and $\operatorname{tg}\delta$ was used in the present study. Thin insulating films made of polyethylene terephthalate with a thickness of 15 μm were positioned one film on

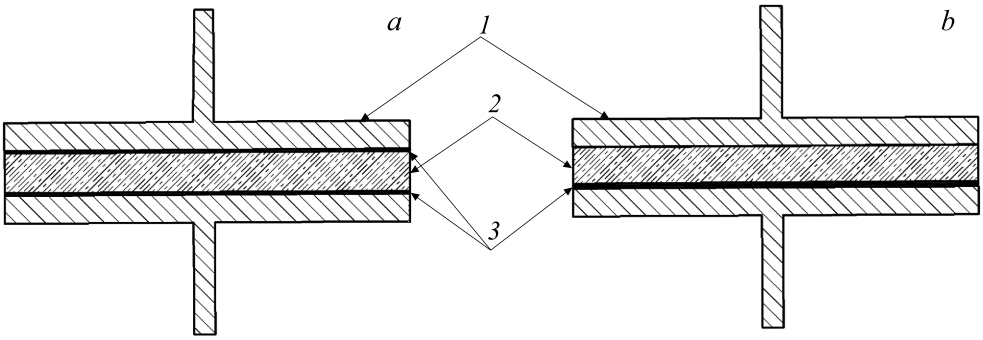

Figure 1. Schematic diagram of the measuring cell. *a* — Insulating films on both sides of the sample (option 1); *b* — films on one side (option 2). *1* — Electrodes, *2* — sample, and *3* — insulating films.

each side of the sample (variant 1) or two films joined together on one side (variant 2; see Fig. 1) between the electrodes of the measuring capacitor and the composite sample under examination. A similar arrangement is found in operation of a composite screen located between the current-carrying conductor and the insulating layer of a high-voltage cable. The samples with high resistivity ($\nu \leq 20\,\%$) were also subjected to measurements of C_x and tg δ without such films (variant 3). The system consisting of the sample and films may be regarded as a circuit with two capacitors connected in series: (1) one containing only the sample between its plates and (2) one containing only two insulating films and, possibly, uncontrolled thin air layers between the electrodes, films, and the sample. Such interlayers may introduce significant errors into the measurement results [11] (especially the results for thin samples or samples with high permittivity ε'). It is easy to verify that the influence of insulating films on the measured value of capacitance C_e also increases when the samples have a small thickness and large values of ε'.

The influence of insulating films and air interlayers on experimentally measured capacitance C_e of the sample–insulating films system was taken into account in the following way:

$$\frac{1}{C_e} = \frac{1}{C_x} + \frac{1}{C_i},$$

which yields

$$C_x = C_e\left(1 + \frac{C_e}{C_i - C_e}\right),$$

where C_x is the capacitance of the capacitor containing only the sample between its plates and C_i is the capacitance of the capacitor containing only two insulating films between its plates. The values of ε' were calculated as $\varepsilon' = C_x h/(\varepsilon_0 S)$, where h is the sample thickness.

Figure 2 shows the obtained dependences of effective permittivity ε' on carbon black content.

It follows from the presented results that the $\varepsilon'(\nu)$ dependence has an initial section with a shallow slope in the region of low concentrations. The value of ε' increases sharply in the percolation region, but further growth of ε' with ν at $\nu > 25\,\%$ is slower. Note that a $\varepsilon'(\nu)$ dependence of a similar nature was observed at a frequency of 50 kHz. Calculations of the $\varepsilon'(\nu)$ dependence of effective permittivity on concentration based on both the Maxwell–Garnett approach and the Bruggeman approach do not provide a satisfactory agreement with the experimental data.

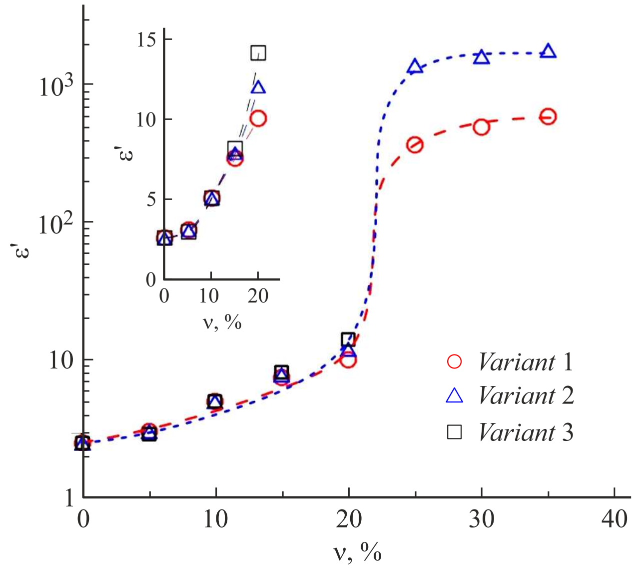

Figure 2. Dependence of effective permittivity ε' on concentration of carbon black ν for different C_e measurement variants.

Figure 3 shows the dependence of conductivity on the concentration of carbon black. It follows from the comparison of dependences $\varepsilon'(\nu)$ and $\sigma(\nu)$ shown in Figs. 2 and 3 that they are correlated qualitatively. Experimental dependence $\sigma(\nu)$ agrees fairly closely with the one calculated according to the following expressions [1]:

$$\sigma_1 = (\nu - \nu_c)^t \quad \text{if} \quad \nu > \nu_c,$$

$$\sigma_2 = (\nu_c - \nu)^{-s} \quad \text{if} \quad \nu < \nu_c,$$

which are derived from the classical percolation theory. Here, ν_c is the critical concentration and t and s are the

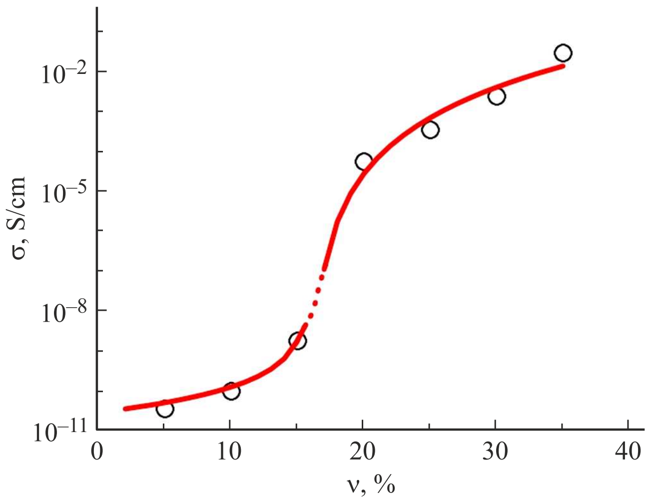

Figure 3. Dependence of conductivity on the concentration of carbon black. Dots and curve sections correspond to experimental and calculated data, respectively.

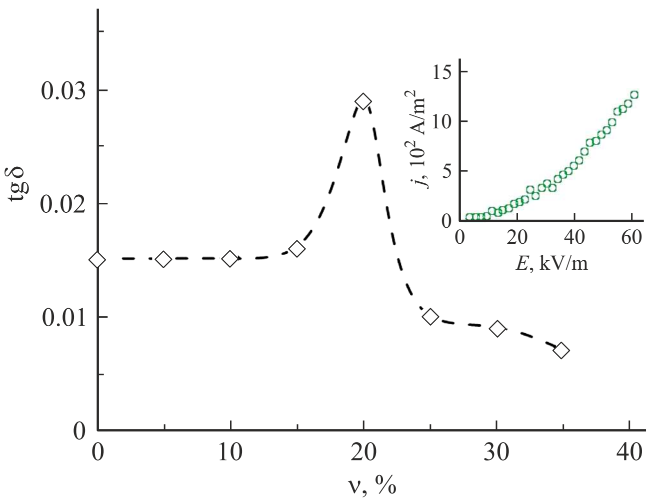

Figure 4. Dependence of loss tangent on the concentration of carbon black. The inset shows the current–voltage curve for a sample with carbon black concentration $\nu = 20\,\%$.

critical indices that are equal to 4 and 1.5, respectively, in the present case.

The dependence of dielectric losses $\mathrm{tg}\,\delta$ on the carbon black content differs significantly from the $\varepsilon'(\nu)$ dependence and is non-monotonic in nature (Fig. 4). At $\nu = 20\,\%$, which is close to the percolation threshold ($\nu_c \approx 17\,\%$), $\mathrm{tg}\,\delta$ increases to ~ 0.03 and reaches its maximum. At higher concentrations ($\nu = 25{-}35\,\%$), $\mathrm{tg}\,\delta$ decreases to 0.015. This variation of $\mathrm{tg}\,\delta(\nu)$ was reproduced in three series of samples. One of the possible mechanisms behind the observed increase in dielectric losses at $\nu = 20\,\%$ is related to the fact that the conductivity increases significantly at such concentrations and the conductivity component induced by field emission of electrons from the surface of carbon black particles with subsequent tunneling becomes dominant. This, in turn, may be associated with certain specific features of energy dissipation processes leading to an increase in losses. Field emission is characterized by a nonlinear current-voltage curve specified by the Fowler–Nordheim relation [12], which agrees with the experimental data for the sample with $\nu = 20\,\%$ shown in the inset of Fig. 4.

One intriguing result is the discovered dependence of ε' on the presence of two insulating films and their positioning on one side or both sides of the sample. While there is virtually no noticeable difference in C_x and, consequently, ε' values at low concentrations, this difference becomes evident at carbon black concentrations upward of $\nu = 15\,\%$. If insulating films are lacking, an even greater increase in C_x and, accordingly, ε' was observed, which is especially noticeable in the composite with $\nu = 20\,\%$ (inset in Fig. 2). The increase in ε' may be attributed to the growing influence of spatial charge in the sample volume, which arises due to the emission of electrons from the electrode in contact with the sample without an insulating film and their drift motion toward the other electrode and back under the action of an alternating electric field, on C_x. The effect of this factor is equivalent to shortening of the effective interelectrode distance.

Thus, the following conclusions may be made.

(1) It was found that the effective permittivity of a composite with an ethylene vinyl acetate matrix increases sharply at carbon black concentrations corresponding to the percolation region. The concentration dependences of permittivity and conductivity of composites are correlated qualitatively.

(2) The observed maximum of dielectric losses near the percolation point may be attributed to the fact that the dominant contribution to conductivity at such concentrations is produced by the mechanism of field emission of electrons from the surface of carbon black particles with subsequent tunneling. This, in turn, is associated with certain specific features of energy dissipation processes leading to an increase in losses.

(3) A significant dependence of effective permittivity on the design of measurements of the capacitance of the capacitor with the sample was found at both examined frequencies (50 Hz and 50 kHz). The presence or lack of thin insulating films on one side of the sample or both its sides has a significant influence on the capacitance and, consequently, the value of permittivity. This factor has virtually zero effect at low concentrations of carbon black, but becomes increasingly significant at concentrations upward of the percolation threshold.

Conflict of interest

The authors declare that they have no conflict of interest.

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