INFLUENCE OF A POLYMER MATRIX ON THE ELECTRICAL PROPERTIES OF POLYMER COMPOSITES BASED ON VARISTOR CERAMICS

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Polymer composites with semiconductive filler based on nonlinear zinc oxide ceramics were obtained. Polyethylene or polypropylene was used as a polymer. It was shown that the volt-ampere characteristics of the composites were nonlinear. It was found that for both composite compositions an increase in the filler volume fraction led to an increase in electrical conductivity due to an increase in the number of channels for electric current flow. The temperature dependences of the electrical conductivity of composites were studied in the temperature range 20 – 70 °C. It was shown that for a composite in a warehouse that included polyethylene the temperature coefficient of resistance was positive. But for a composite with polypropylene, the temperature coefficient of resistance was negative.

Keywords: posistor, polymer, polyethylene, varistor ceramics, temperature coefficient of resistance.

Received 04.11.2021; Received in revised form 07.12.2021; Accepted 10.12.2021

1. Introduction

Polymer composites are heterogeneous materials in which the conductive phase is used as a filler in a polymeric dielectric matrix. Self-resetting fuses of the Polyswitch type based on the polyethylene-graphite composite have already been created [1-3]. For giving polymeric composite special electrical properties, other conductive fillers were used in addition to carbon. The use of metal oxides as a conductive filler is relevant because allows the synthesis of materials with unique characteristics. This allows to expand the existing range of electronic devices significantly. For example, in [4] vanadium dioxide was used as a filler, in which a semiconductor-metal phase transition is observed. It was shown [5] that polyethylene-ZnO composites have a nonlinear current-voltage characteristic (CVC). Oxide varistor ceramics can also be used as a filler for polymer composites. To do this, ceramics is first crushed to a powder state with a particle size close to the size of individual grains in ceramics and then mixed with a polymer. The composites obtained in this way have a non-linear current-voltage characteristic and, as a rule, a positive temperature coefficient of resistance. In [6] the results of the synthesis and study of composites, which are a system of particles of highly nonlinear varistor ceramics based on zinc oxide in a polyethylene matrix, were presented. Composite polyethylene-varistor ceramics based on WO_3 [7], in addition to the nonlinear CVC, also had a very high positive temperature coefficient of resistance. This work is devoted to the study of electrical properties of polymer composites with a conductive filler based on nonlinear zinc-oxide ceramics with different polymer matrices. Low density polyethylene or polypropylene were used as a matrix.

2. Samples and measurements

The low-density polyethylene (LDPE) [8] (brand 15803-020), polypropylene granules and powder of crushed zinc-oxide varistor ceramics were initial components for the manufacture of composites. CH2-1 [9] varistors without electrodes were crushed and used as a composite filler. The volume percentage of filler (V_d) ranged from 10% to 84% for the composite with a polyethylene matrix and from 10% to 30% for the composite with a polypropylene matrix. During the manufacture of the composite, the required amount of polymer granules and varistor ceramic powder was loaded into a test tube and subjected to heating until the polymer turned into a viscous-flow state. The mixture was thoroughly mixed and allowed to cool. After that, the composite was released from the test tube and mechanically crushed to a particle size of ~0.5 mm. The powder was pressed under a pressure of ~1 MPa. At the same time, electrodes from a fine copper mesh were pressed onto the upper and lower surfaces of the samples. Then the samples were subjected to hot pressing at 130 °C at a pressure of ~ 0.1 MPa for one hour. In this way, mechanically strong composite samples with a diameter of 12 mm and a thickness of 1.5 – 3 mm were synthesized. To measure the temperature dependence of the conductivity, the samples were placed in a thermal cabinet where the temperature varied from room temperature to 80 °C. The rate of temperature increase was 0.75 °C/min. The electric field strength during measurements was from 2 V/mm to 10 V/mm in the linear section of the CVC. The temperature coefficient of resistance was calculated from the temperature dependences of the conductivity, according to the ratio:

$$R = R_o \cdot (1 + \alpha \Delta t), \quad (1)$$

where R — resistance; R_o — initial resistance; α — temperature coefficient of resistance; Δt — temperature increase.

3. Experimental results and discussion

Dependences of the electrical conductivity of composites on the volume fraction of the conductive filler are shown in Fig. 1, 2. For polymer-ceramic composites, both with the use of polyethylene (Fig. 1) and with the use of polypropylene (Fig. 2) increasing the volume fraction of the filler leads to an increase in the electrical conductivity of the composite. This is due to an increase in the number of channels of electric current. For the polyethylene-ceramic composite, a sharp jump in electrical conductivity is observed at low filler concentrations (it is percolation threshold) [10-12]. The volt-ampere characteristics of the synthesized composites were weakly nonlinear ($\beta \approx 2 – 4$).

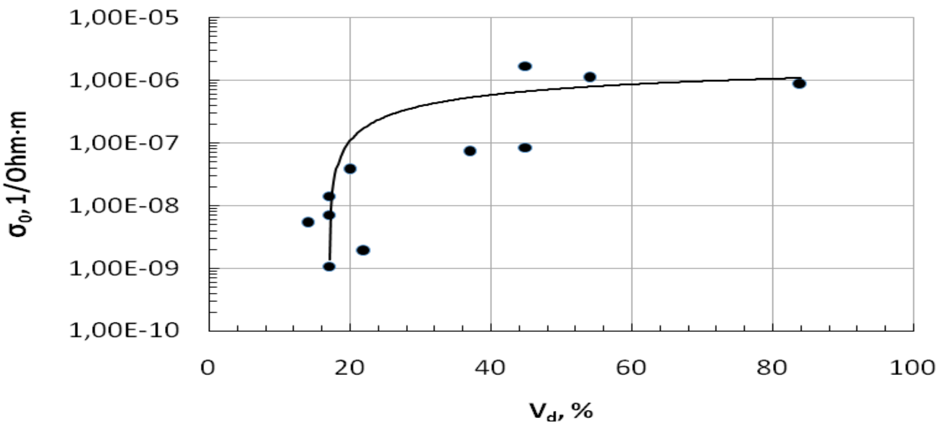

Fig. 1. The dependence of the conductivity of polyethylene-varistor ceramics composites on the filler content (points – experimental data; line – approximation).

The temperature dependences of the specific electrical conductivity of the polymer-varistor ceramic composite were measured in the temperature range of 20 – 70 °C. From Fig. 3 it can be seen that the conductivity in polyethylene samples decreases with increasing the temperature. Therefore, for the composite polyethylene-varistor ceramics, the temperature coefficient of resistance (TCR) is positive. This process occurs due to the high coefficient of linear expansion of the polyethylene matrix in comparison with the particles of varistor ceramics. In this case, the average distance between ceramic particles increases, which leads to a decrease in the conductivity. For polypropylene-ceramic composite (Fig. 4) the temperature coefficient of resistance is negative. The value of TCR (α) was calculated according to (1) in the temperature range of 20 – 70 °C. TCR for the polyethylene-varistor ceramics composite is 0.36 °C^{-1} and for the polypropylene- varistor ceramics is – 0.017 °C^{-1}.

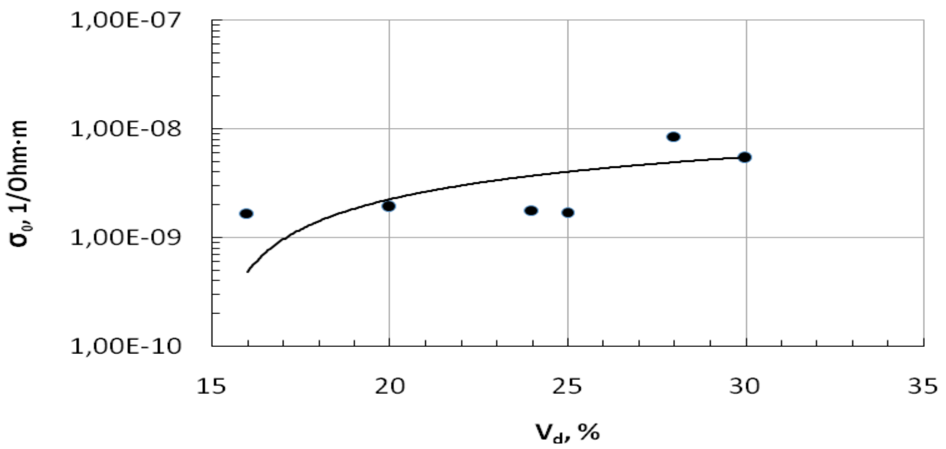

Fig. 2. The dependence of the conductivity of polypropylene-varistor ceramics composites on the filler content (points – experimental data; line – approximation).

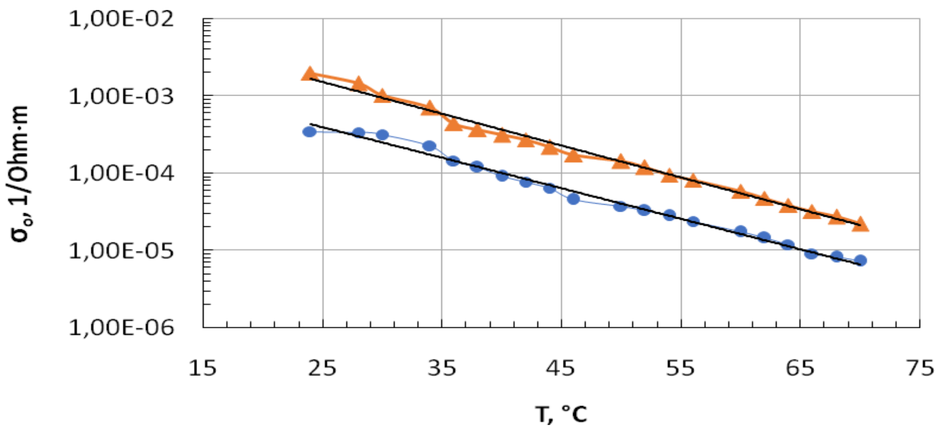

Fig. 3. Temperature dependences of the conductivity of the composite polyethylene-varistor ceramics (triangles – V_d = 37%, squares – V_d = 45%).

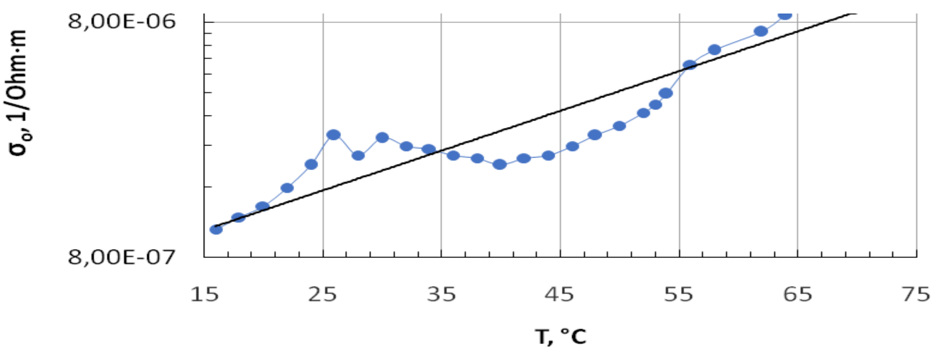

Fig. 4. Temperature dependences of the conductivity of the composite polypropylene-varistor ceramics (V_d = 20%).

The polypropylene matrix hardly expanded. For a polypropylene-based sample, the electrical conductivity increases with increasing temperature due to the fact that the main factor in the change in electrical conductivity is the increase in the electrical conductivity of the semiconductor filler. In the case of samples based on polyethylene, the main factor in the electrical conductivity change is the expansion of the polymer matrix. The difference in the behavior of the temperature dependences of conductivity for composites with polyethylene and propylene matrices can be explained by different values of the temperature coefficient of linear expansion of these polymers. For polyethylene, this parameter is much larger ($22 \div 55 \cdot 10^{-5}$ °C^{-1}) than for polypropylene ($12 \cdot 10^{-5}$ °C^{-1}).

4. Conclusion

Composites with a semiconductive filler based on non-linear zinc oxide varistor ceramics have been obtained and studied. Polyethylene or polypropylene was used as a polymer matrix. CVC of composites is non-linear. It is shown that the increase in the volume fraction of the filler leads to an increase in the electrical conductivity of the composite by increasing the number of channels of electric current. The decrease in the electrical conductivity of the polyethylene-varistor ceramic composite with increasing temperature is explained by the expansion of the polymer matrix and the rupture of the conductive channels between the conductive grains of the varistor ceramic. An increase in the electrical conductivity of the polypropylene-varistor ceramic composite with increasing temperature is explained by an increase in the electrical conductivity of the semiconductor filler. The value of the temperature coefficient of linear expansion of the polymer is of decisive importance for the sign of the temperature coefficient of resistance of the composite.

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