Electrophysical Characteristics of Composite Nonlinear Resistors Based on Polymer and Silicon

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Abstract—This work presents the results of studies of the volt-ampere characteristic, resistivity, as well as infra-red spectra and X-ray diffraction patterns of composite resistors (varistors) based on polypropylene and monocrystalline silicon. The effect of the composition of the components of the composite on the volt-ampere characteristics, the resistivity values, and the nature of the infrared and X-ray spectra was found.

INTRODUCTION

At present, to protect microelectronic devices, and in view of their transition to nanotechnologies, the need for the low-voltage limiters of overvoltage will increase. Therefore, the development of low-voltage non-linear resistors—varistors with various combinations of composite materials is of high priority [1–7].

In addition, the structure of polymer materials is the main factor that determines their physical and chemical properties. The development of physical chemistry and technology of composite materials, which are multicomponent systems and are largely filled linear and network polymers, requires us to clarify our concepts of the character of their close ordering and their supermolecular order. In this context, the X-ray diffraction of X-ray radiation is a of leading method.

This work studies the effect of the volume percent content of a filler on the volt-ampere characteristics, the resistivity value (at the fixed voltage), and on the nature of infrared and X-ray spectra of the composite nonlinear resistors (varistors) based on polypropylene and monocrystalline silicon.

EXPERIMENTAL

We used semiconducting monocrystalline silicon (p-Si) and polypropylene (PP) as the composite components. To obtain the resistors, the monocrystalline silicon was preliminarily powered in a ball mill with porcelain balls up to $60 \mu m$ and less. The resistors were formed from a homogeneous blend of the components by hot pressing at a temperature 180°C and a pressure of 15 MPa. The composition of the components of the composite varied in a wide range (0.01–60% Si and 99.99–40% PP, respectively). The samples were $150 \mu m$ thick. All samples were studied for the dependences of the volt-ampere characteristic and resistivity, as well as the infrared spectra (IR-Fourier spectrometer-Vector-22) an X-ray pattern on the volume percent composition of the filler (Si). The parameters studied were measured at room temperature ($T = 293$ K).

Based on the experimental results (Figs. 1–6), the effect of Si percent composition on the volt-ampere characteristic, the value of resistivity, IR-spectra, and X-ray patterns of composites was found. As can be seen from Fig. 1, the dependence of the resistor value of current on the applied voltage, except for the PP-100%, for all samples is nonlinear, and it is mainly due to the supplied voltage that the current value via varistor increases and changes by 2–3 orders. In addition, depending on the percent composition of the filler, the voltage of transition of VAX from linear to nonlinear region (transition voltage V_{tr}) changes.

The dependence of resistivity on the percent composition of the filler (Si) conventionally can be divided into two sections (Fig. 2).

At the initial section 1, the value of resistivity (ρ) is high, and up to Si-10%, it is mainly determined by the polymer resistance. In section 2, the value of resistivity (ρ) with an increase in the percent composition of the filler is abruptly decreased, and with a further increase in the percent composition of the filler Si $\geq$ 30% the value of resistivity remains almost constant.
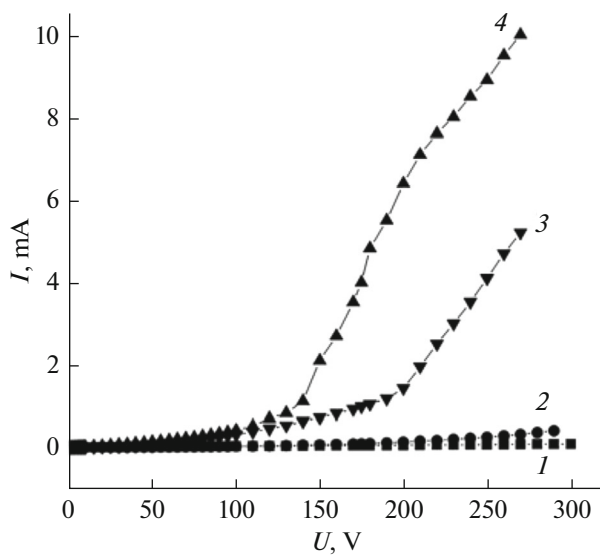
Fig. 1. Volt-ampere characteristics of composites with different Si-composition. (*1*) 100% PP; (*2*) 40% Si + 60% PP; (*3*) 50% Si + 50% PP; (*4*) 60% Si + 40% PP.
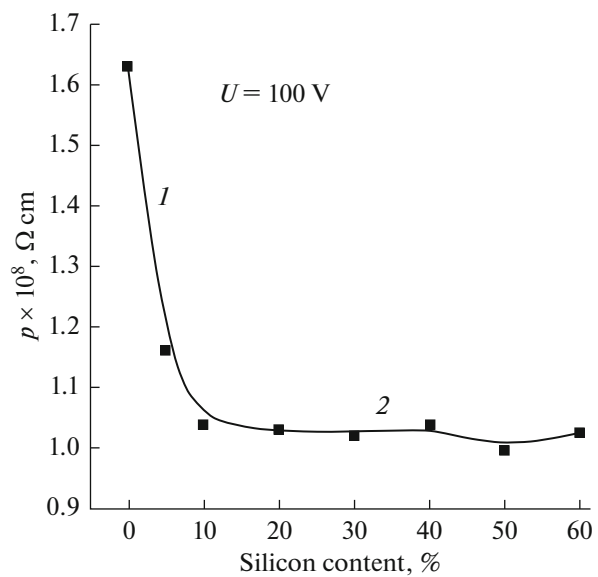

Fig. 2. Dependence of composite electroconductivity on silicon content.

The analysis of the IR-spectra (Fig. 3) shows that for polypropylene with the filler, compared to the sample of (100% PP), the intensities of the absorption bands typical for the symmetrical CH_2 (1435 cm^{-1}) and CH_3 (1378 cm^{-1}) and asymmetrical deformation oscillations of CH_3 (1454 and 1400 cm^{-1}) and peculiar to pure polypropylene, decrease significantly.

The X-ray pattern shows that the dependence of the intensity of reflexes that is relevant to various Miller indices (*hkl*), with an increase in the percent composition of the filler sharply increases up to the maximum value.

The diffraction patterns were taken using an XRD D8 diffractometer (firm Bruker) with CuK_{α}-irradiation.

RESULTS AND DISCUSSION

Before we discuss the experimental results, we note that according to our data and those of other authors [2–7], the main reason for the observed nonlinearity of VAC are the potential barriers that occur between the particles of a filler (silicon) and polymeric matrix. In this case, the charge carriers transfer in a composite can occur (1) by tunneling through the potential intercrystallite and interphase barriers, (2) via the direct contacts between the particles of silicon, and (3) by means of emission of the carriers through the barriers between the particles of the filler.

In [8, 9] the authors show that in the conductivity of compositions a significant role belongs to the average number of contacts per a single particle. In addition, as is known from electrotechnics, the electric current between two conducting substances can pass both at their contact and in the presence of a thin dielectric film between them.

Thus, the dependence of resistivity of the composite on the percent composition of the filler Si can be explained as follows. For low contents of silicon in the composite, the average number of contacts per particle is low, so the number of contacts will also be low. In this case, the composite resistance will be determined mainly by the resistance of polymer (matrix), and conductivity will be hopping (section 1). An increase in the percent content of Si leads to: (1) an increase in the average number of contacts and (2) a decrease in the width of the potential barrier between the particles of silicon and polymer. This, in its turn, leads to an exponential increase in the number of carriers through the barrier. As a result, the composite conductivity increases and, correspondingly, its resistivity decreases (section 2). Further growth of silicon content causes the formation of continuous conducting chains from silicon particles. For this reason, further on the conductivity of the composite will be determined by the conductivity of the silicon particles. It is noteworthy that the degree of the structural perfection of polymers can vary in a wide range depending on the polymer nature, on its prehistory and external conditions. In addition, the appearance of the diffusion maxima on diffractograms are caused by scattering on the disordered regions of polymer. Thus, we can conclude that the structure of this polymer has a two-phase character. According to the simplified presentations, the two-phase nature of the structure of crystallizing polymers is caused by the presence of entirely amorphous regions and regions with a crystalline structure in their volume. A quantitative characteristic of the two-phase structure of these materials is their degree of crystallinity, which
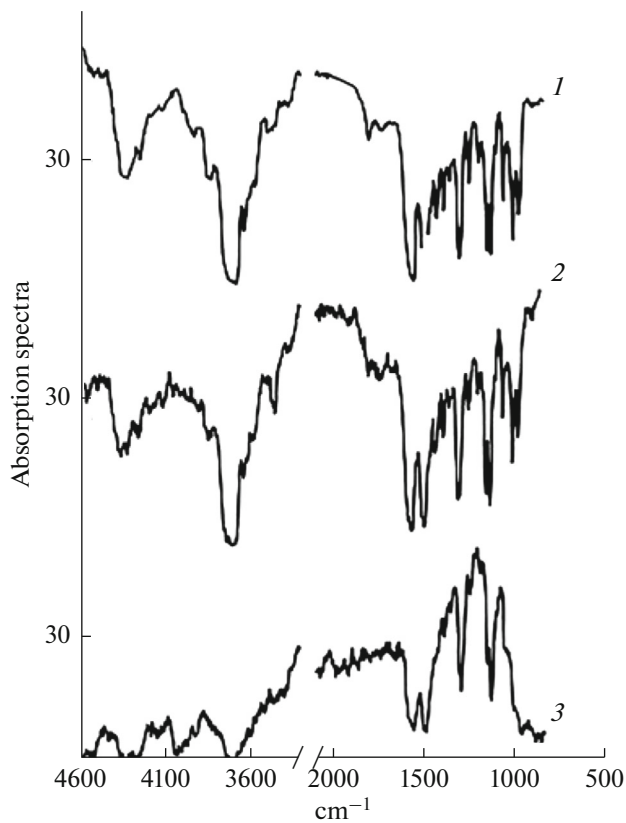
Fig. 3. Spectra of absorption of composite and its components.

Fig. 4. Dependences of intensity of X-ray pattern of composite for different Miller indices on silicon content. (*1*) $d = 3.13$ Å (111); (*2*) $d = 1.92$ Å (220).

defines the ratio of crystalline and amorphous areas in the material.

At present, many various methods have been developed to estimate the degree of crystallinity of materials, using the measurements of density, infrared spectroscopy [10−13], the spectra of nuclear magnetic resonance, and other means. The most commonly used are the methods that employ the data of wide- and narrow-angle X-ray diffraction [14]. The use of X-ray diffraction suggests the validity of the following statements: (1) the integral intensity of each crystalline reflex is proportional to the composition of a corresponding crystalline phase, (2) the intensity of a curve of an amorphous scattering of the material of a certain phase in each point is proportional to the quantity of the material of this phase, and (3) the total contribution of scattering the material of a certain phase (crystalline or amorphous) is an integral value.

Note that the simplest method to define a relative degree of crystallinity is the Mathews method [11]. It is based on the comparison of the degree of crystallinity with the ratio of the area occupied by the crystalline X-ray reflexes (S_{cr}) to the overall area occupied by the curve of the coherent scattering ($S_{cr} + S_{am}$). Taking the latter into account, the degree of crystallinity of the composite was determined using (1):
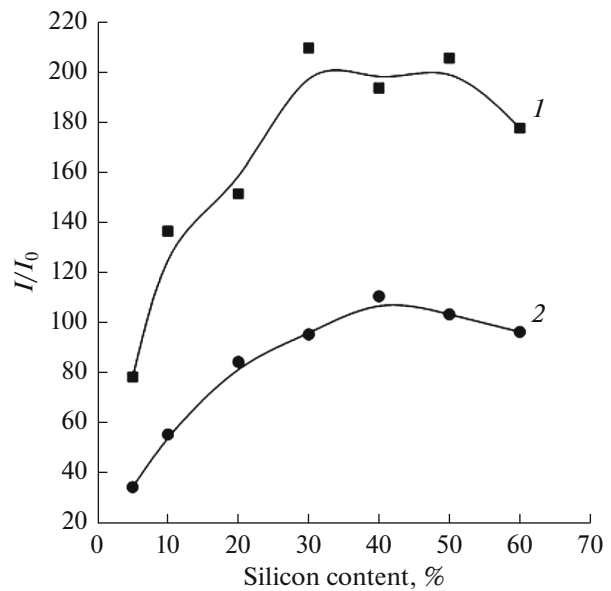
$$X_{cr} = S_{cr}/(S_{cr} + S_{am}). \qquad (1)$$

In addition, according to [15], the intensity of scattering of the X-ray radiation is determined mainly by the difference in densities of crystalline and amorphous zones. In fact, the crystalline zones of polymer are inaccessible to foreign atoms. Therefore, the latter can be accumulated in the amorphous areas of the polymer. In [15], there is a formula, which describes the ratio between the densities of amorphous and crystalline regions and the intensity of scattering of the X-ray radiation *I*:

$$I \sim A(\rho_{cr} - \rho_a)^2, \qquad (2)$$

where *A* is the constant value; ρ_{cr} and ρ_a are the densities of crystalline and amorphous regions of polymer, respectively. The observed experimental dependence between intensity (*I*) of the X-ray radiation and the volume percent composition of the filler (Si) can be explained as follows (see Figs. 4, 6).

In our opinion, the reasons for the growth of the crystallinity of the composite are that (a) on the one hand, the filler is a monocrystalline silicon, and (b) on the other hand, foreign additives cannot access the crystalline area of the polymer, and they can only accumulate in the amorphous region of the polymer. With an increase in the percent composition of the filler (silicon) the amorphous share will decrease and that of the crystalline composite will increase. Then, according to (2), the cofactor ($\rho_{cr} - \rho_a$) and, as a consequence, the intensity (*I*) of the X-ray radiation must increase (see Fig. 4), which is supported by the experimental results.

The growth of the degree of the composite crystallinity with an increase in the percent composite of the
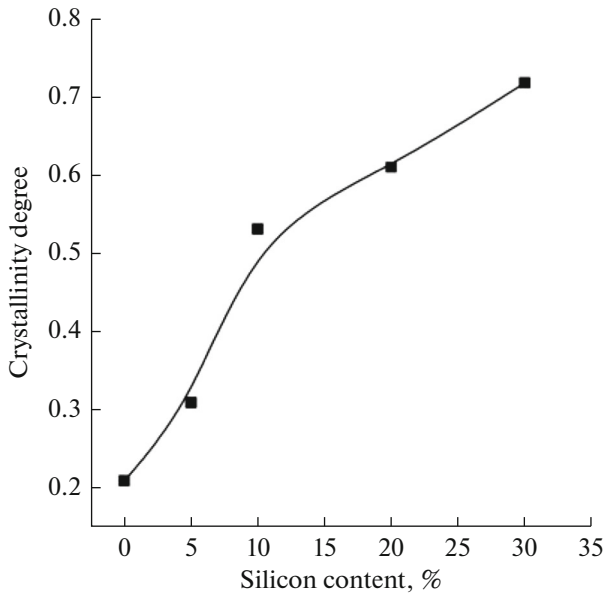
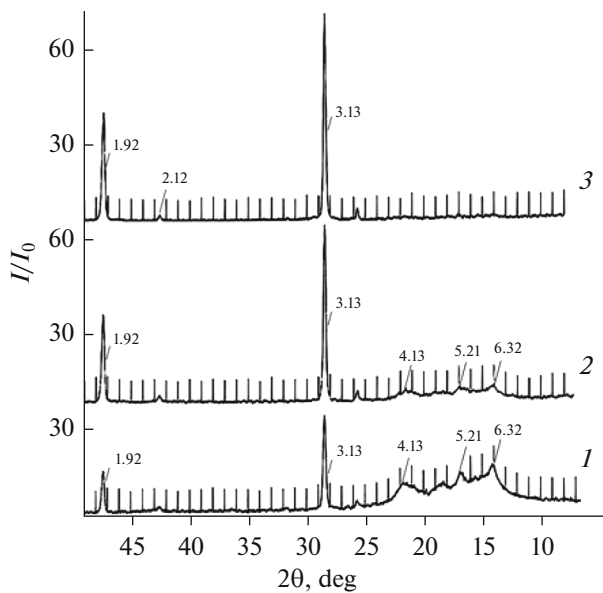**Fig. 5.** Dependence of crystallinity degree on silicon content.

Fig. 6. Diffractogram of composites with different composition of components Si + PP. (*1*) 5% Si—95% PP; (*2*) 20% Si—80% PP; (*3*) 60% Si—40% PP.

tures in the intercomponent regions. A comparatively minor range of changes in the index of crystallinity during mixing attests to the insignificant mutual effect of the components in the above systems.

CONCLUSIONS

The analysis of the experimental results shows the effect of the percent composition of the filler on the electrophysical characteristics and on the Infrared spectra and X-ray reflexes of the composite. Technology has been developed for obtaining the composite varistors based on monocrystalline silicon and polymer material, which in the future will make it possible to create various low voltage, low energy-intensive, cheap composite varistors for the in microelectronics and other areas.

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filler is also confirmed by the dependence of the composite crystallinity degree calculated using formula (1) (Fig. 5). As can be seen from this figure, with an increase in the percent composition of silicon the degree of the composite crystallinity grows.

The observed decrease in intensity after 40% of Si (Fig. 4) clearly may be connected with the change in the kinetics of crystallization of polymer in the presence of the second component and with certain increases in the composition of the disordered struc-

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