

POSISTOR ELEMENTS BASED ON CERESIN–NANOCARBON COMPOSITES

A.Yu. Lyashkov*, A.S. Tonkoshkur, S.F. Lyagushyn

*Oles Honchar Dnipro National University, Dnipro, Ukraine
e-mail: alexdnu@ukr.net*

Experimental results of the development of self-healing fuses based on ceresin–nanocarbon composites are presented. The technical framework for the applicability of industrial resettable fuses based on polyethylene is justified. Good prospects of using composites based on ceresin to create low-temperature posistor elements with the aim of providing current protection for solar cells is shown.

Keywords: PolySwitch, posistor, composite, carbon black, ceresin, fuse, solar array.

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1. Introduction

Carbon-filled polymer composites are used as posistor elements to create self-healing PPTC fuses (PPTC, polymeric positive temperature coefficient) of the PolySwitch type [1-3].

The basic functional property of PPTC fuses is a jump-like (by several orders of magnitude) increase in electrical resistance when a certain threshold temperature is reached and a return to the initial highly conductive state when the temperature is lowered [4, 5].

Such fuses effectively protect power supplies in the event of a short circuit or overcurrent. In particular, they have found application as devices for electrical and thermal protection in batteries and galvanic power supplies [6-10].

So, PolySwitch tape elements are designed to protect nickel-cadmium, nickel-hydride metal and lithium-ion batteries used in cellular telephones, laptop computers, and other portable electronic equipment.

The advantages of such structures based on polymer composites with nanocarbon fillers include:

- relatively small production costs and miniature sizes;
- resistance that is close to the resistance of metals at a temperature below the switching temperature and close to the resistance of an insulator at a temperature above it [4, 5];
- the possibility of implementation in the form of discrete elements and continuous tape films [8, 9] (which is important when performing isolation of a local defective region of a single PV (photovoltaic) element);
- the possibility of temporary disconnection of individual heated inactive (e.g., shaded) components of the solar array from a common electrical circuit [4, 5, 11].

Recently, as one of the new areas of application of posistor elements based on the nanocomposites under consideration, they are used to solve the problems of constructing systems for protecting components of photovoltaic systems of solar cells from electrical overloads [11, 12]. The general scheme and conditions for the use of resettable fuses to limit the current in parallel connections of photovoltaic modules by connecting a separate PPTC fuse in series with each module are justified [13]. It is shown that the series connection of self-healing PolySwitch fuses in photovoltaic modules when connected in parallel allows them to prevent contingencies of the complete loss of the electrical energy generated by this unit, which occurs when a short circuit in one of its modules. The use of such fuses ensures the shutdown of a faulty (short-circuited) photoelectric module. The total power loss of the unit in this situation is determined by a decrease in its current by an amount equal to the sum of the current of one photovoltaic module and the support current of the fuse in the low-conductive state.

The development of thermosensor fuses on the basis of considered PTC polymer structures to prevent local overheating ("hot spots") in PV solar cells [11, 12, 14] is one of the new ways of posistor structure application.

In particular, it is proposed to use the basic functional property of self-healing fuses – a jump-like increase of resistance by several orders upon reaching a certain limiting temperature and returning to the initial highly conductive state with decreasing temperature. At the same time, the following should be noted: the operating temperature of the most common types of commercial PPTC fuses at present is about 80 °C, and a significant change in resistance is observed at even higher temperatures of 90–125 °C [15]. Moreover, the maximum operating temperature of the PV modules does not exceed 80 °C [11]. To some extent, this situation limits the widespread use of PPTC fuses as elements of protection against overheating, especially if the cause of overheating is a temporary one. In this regard, the development of PPTC fuses with a low operating temperature [11, 12, 16] seems to be the most important, which is considered in this paper.

In the present work an approach based on the use of a ceresin composite, which has a lower temperature from the crystalline to amorphous state, as a matrix polymer is used to solve the above problem [17]. Particular attention is paid to studying the effect of variations in technological schemes for the manufacture of these resistor nanocomposites on their electrical properties.

2. The experimental technique

2.1. Samples

The following components were used as initial ones for manufacturing the composite: carbon black, grade N550 (according to ASTM D1765) with a particle size of 39–55 nm, ceresin, grade 65, and polyvinylidene fluoride (PVdF).

The synthesis of the studied composites was carried out according to the technological schemes described below, similar to the general manufacturing technology of self-healing fuses of the PolySwitch type [1, 2].

Technological scheme No. 1 included:

- mixing ceresin with carbon black in the required proportion;
- heating the mixture until ceresin melting and its transition to a state with low viscosity, mixing the components;
- cooling of the mixture and its grinding;
- pressing the resulting mixture with a hydraulic press in a press form at a pressure of 10 MPa in the form of cylinders 3-4 mm high and 12 mm in diameter with simultaneously pressing electrodes made of a thin copper mesh into the end surfaces.

In accordance with scheme No. 2:

- ceresin was dissolved in 1-Methyl-2-pyrrolidone (N-methyl-2-pyrrolidinone (NMP));
- the required amount of carbon black was added to the resulting viscous solution and mixed;
- the material synthesized in this way was applied in the form of disks with a diameter of 5 mm and a thickness of 1-2 mm between two electrodes of a thin copper mesh and allowed to dry under atmospheric conditions.

Technological scheme No. 3 repeated the technology No. 2 with one difference – polyvinylidene fluoride (PVdF) dissolved in 1-methyl-2-pyrrolidone was added to the resulting mixture.

2.2. Experimental details

The temperature dependences of the electrical resistivity and current-voltage characteristics (curve I-V) were measured by standard methods. For this, the samples were placed in a protective chamber. The data were recorded after the thermodynamic

equilibrium of the test sample with the environment was established. Electrical measurements were carried out with using laboratory power supplies TV-2, TES-42 and digital voltmeters V7-27/A1.

In order to control the degree of crystallinity of ceresin, an X-ray phase analysis (XRD) was performed with a DRON-3M instrument (Burevestnik, Russia) using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$).

The study of dielectric characteristics in the radio frequency range (from 50 kHz to 10 MHz) was performed using a BM-560 Q-meter. Investigations of near-electrode phenomena have shown that the measured electrical values are determined by the bulk properties of the samples.

3. Experimental results and discussion

3.1. Structure and physical properties

Ceresin has a fine crystalline structure and is a mixture of saturated hydrocarbons with the number of carbon atoms in the molecule from 36 to 55. Its molecular weight is about 700. It consists mainly of weakly branched isoalkanes and naphthenes with a long side chain. The X-ray phase analysis of ceresin grade 65 confirms its crystalline structure (Fig. 1).

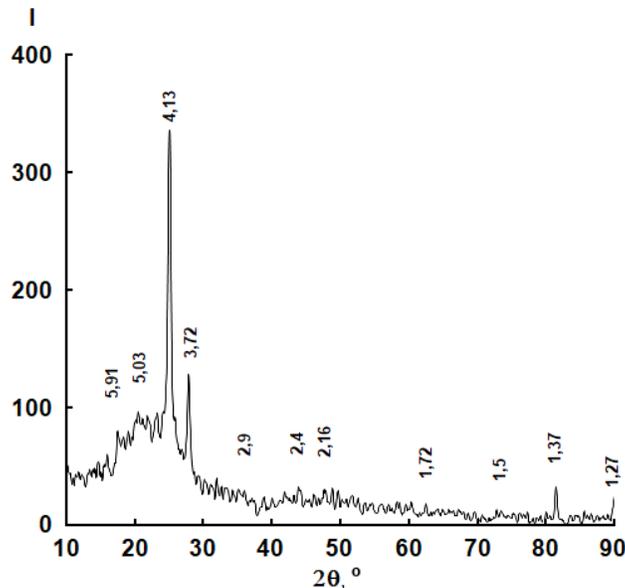


Fig. 1. XRD of ceresin grade 65 ($\text{CuK}\alpha$ radiation).

Samples made with using technologies No. 1-3 were also subjected to X-ray phase analysis in order to check the effect of the technique and additives on the crystallinity degree of ceresin. It was found that a noticeable decrease in crystallinity was not observed. When polyvinylidene fluoride composite was added to the material, line broadening occurred, this, according to the Scherrer formula [18], was interpreted as a decrease in the average size of ceresin crystals.

3.2. Electrical properties

3.2.1. Temperature dependences of electrical conductivity

The temperature dependences of the specific resistance (ρ) of composite samples with various volume fractions of carbon manufactured using technology No. 1 are presented in Fig. 2. With increasing filler content, ρ decreases. An increase in

temperature leads to an increase in resistivity by more than two orders of magnitude in the temperature range 17–55 °C. However, with a further increase in temperature, softening and swelling of the composite were observed.

To improve the manufacturability of the composite, dissolution of ceresin in 1-methyl-2-pyrrolidone was used (flow chart No. 2). This eliminates the operation of melting and pressing. The resistivity gradually increased with increasing temperature (Fig. 3). When approaching the melting temperature of ceresin (65 °C), a sharp transition is observed, apparently related to its melting and increase in the volume of the composite matrix. A similar increase in volume occurs also in polyethylene [19]. Resistance increases approximately 20 times in the temperature range of 21–70 °C. Then ρ stabilizes.

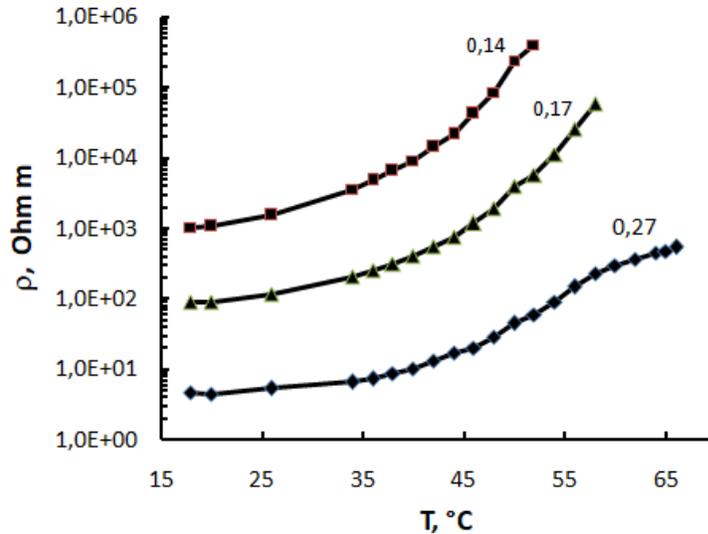


Fig. 2. Temperature dependences of the resistivity of the samples of the composite ceresin–nanocarbon with different volume fractions of the filler (nanocarbon) made by melting the source material (technological scheme No. 1).

Although deformation with increasing temperature was not so pronounced in samples synthesized according to scheme No. 2, an attempt was made to stabilize the mechanical properties of the material by the addition of polyvinylidene fluoride (technological scheme No. 3).

Polyvinylidene fluoride has good mechanical strength, hardness, creep resistance and chemical stability. Its crystallinity degree is 45–55%, melting point 177 °C.

The resistivity of the samples obtained according to scheme No. 3 also showed an increase with increasing temperature (Fig. 4). However, the increase did not exceed one order and was quite monotonous. A large proportion of carbon, as well as for samples manufactured according to technological scheme No. 1, led to a decrease in resistivity. The experimental samples had good mechanical strength up to 90 °C and were rather stable during thermal cycling, however their electrical resistance often changed stepwise complying with the general tendency to increase with increasing temperature.

Such behavior can be explained with the composite structure relaxation. As the temperature rises, ceresin expansion is observed, especially near the melting point, while the matrix formed by ceresin becomes less durable. This leads to the release of mechanically stressed structures of polyvinylidene fluoride and the compression of

certain areas of composite. Similar processes occur at tectonic shifts of the Earth's crust causing earthquakes. This allows us to explain the spasmodic behavior of the temperature dependences of the parameters of ceresin–nanocarbon composite with the addition of polyvinylidene fluoride.

3.2.2. Current-voltage characteristics

The dependences of the current density on the electric field strength of samples made by various techniques are presented in Fig. 5. With an increase in the field strength for samples manufactured by all three technologies, an increase in current was initially observed. Then, upon reaching certain critical strength, the current value begins to decrease. Presumably, this implements the same mechanism associated with the expansion of the polymer matrix as in industrial PPTC fuses based on polyethylene [19].

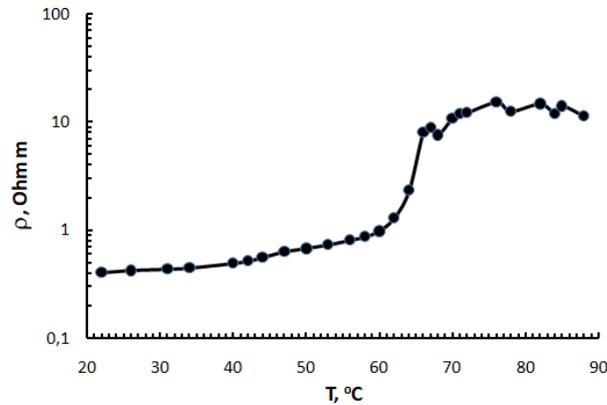


Fig. 3. Temperature dependences of the resistivity of a sample of a ceresin–nanocarbon composite manufactured using a solvent (flow chart No. 2, carbon volume fraction 20%).

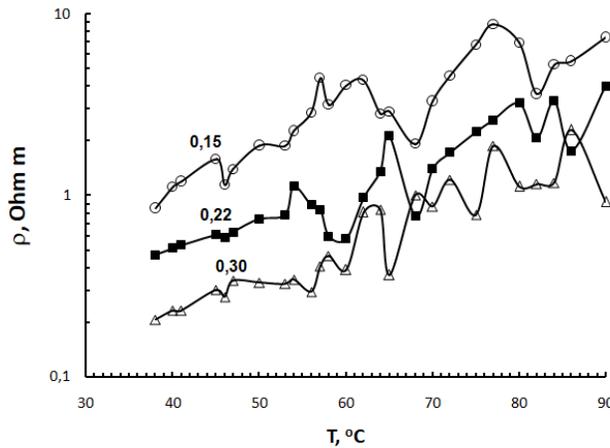


Fig. 4. Temperature dependences of the resistivity of ceresin–nanocarbon composite samples manufactured using a solvent and the addition of polyvinylidene fluoride (flow chart No. 3) with different volume fractions of carbon black.

Fuses manufactured using different technologies are triggered at slightly different electric field strengths, as well as at different current densities through the sample. This indicates both the significant influence of technological factors on the sample properties,

and the need to optimize technology and composition in order to reduce the anisotropy of the composites.

3.2.3. Dielectric permittivity

Typical frequency dependences of the dielectric parameters of the synthesized nanocomposite structures are presented in Fig. 6. As can be seen, the real and imaginary parts of the complex dielectric constant decrease with increasing frequency (Fig. 6), which is typical for inhomogeneous materials [20].

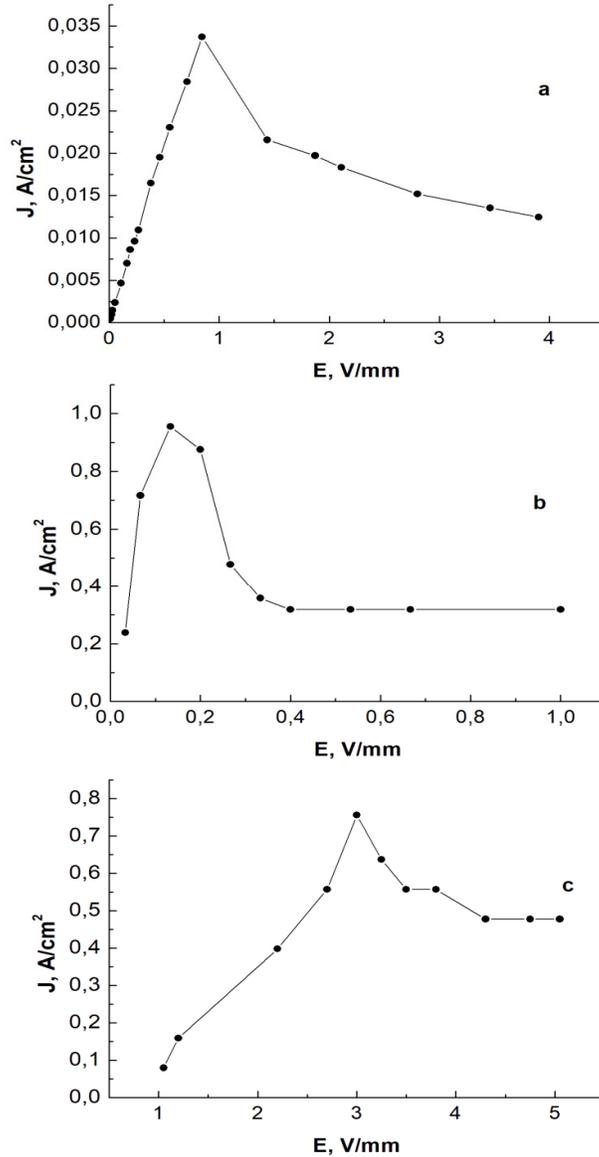


Fig. 5. The dependence of current density on the electric field strength for the samples of the composite ceresin–nanocarbon:

- a – technological scheme No. 1, the volume fraction of carbon is 9%;
- b – technological scheme No. 2, the volume fraction of carbon is 20%;
- c – technological scheme No. 3, the volume fraction of carbon is 15%.

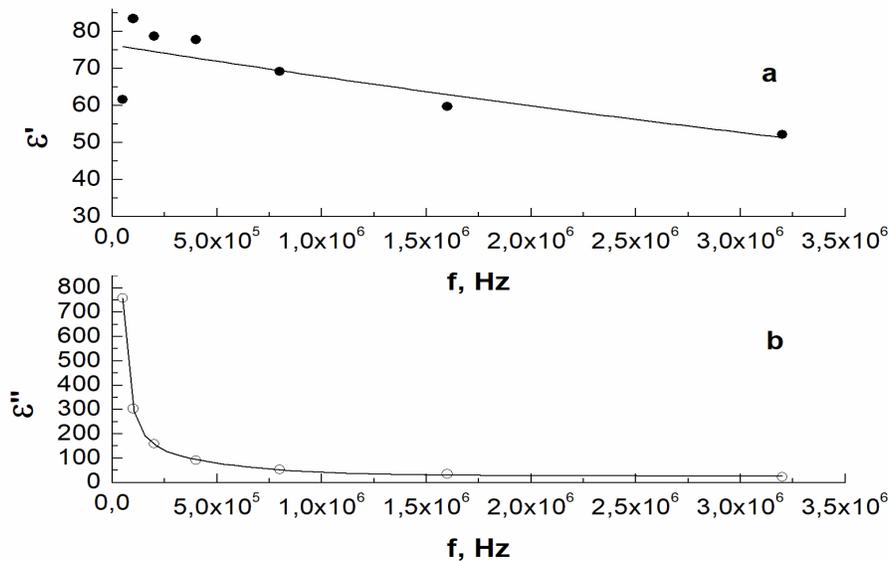


Fig. 6. Frequency dependences of the real (a) and imaginary (b) parts of the complex dielectric constant of a ceresin–nanocarbon composite manufactured by melting the initial material (flow chart No. 1, carbon volume fraction 14%).

Conclusions

1. The use of ceresin as a matrix material of the composite can significantly reduce the switching temperature in comparison with industrially produced self-healing fuses. This makes them promising for the protection of solar cells from local overheating and current overloads.
2. Adding a composite of polyvinylidene fluoride leads to a decrease in the average crystal size of ceresin.
3. The switching mechanism in ceresin–nanocarbon composites is similar to that of polyethylene–carbon composites and is associated with rupture of conductive channels in the process of the polymer matrix expansion during the phase transition from crystalline to amorphous state.
4. Introduction of polymers with a relatively high melting point to the composition allows stabilizing the mechanical properties of the material.

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