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RESEARCH OF THE ELECTRICAL PROPERTIES OF COMPOSITE VARISTORS BASED ON ZnO-POLYMER

Sh.M. Ahadzadeh   A.M. Hashimov   Sh.G. Khalilova

Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan
ahadzade79@mail.ru, ahashimov@azerenerji.gov.az, shahlaganbarova@gmail.com

Abstract- The article describes the electrical properties of composite varistors based on ZnO polymer. To determine the scope of application of composite varistors, the opening voltage and breakdown voltage of composite varistors are determined. It turned out that, the sources of formation of free effective electrons are the beginning the process of electrical destruction. The intensity value is determined before and after modification of the electric discharge. In addition, on the basis of X-ray spectra, a graph was constructed of the dependence of the intensity values on the percentage of filler at various Miller coefficients. An X-ray diffraction pattern was taken for a pure ZnO ceramic varistor. It was determined that the breakdown voltages and the opening voltages of the composites practically coincide. It was also found that the dependence of the intensity value on the percentage of filler does not depend on the Miller coefficients. After modification of the electric discharge composites, the intensity value increases. In the diffraction patterns, reflections for ZnO used as a filler were observed.

Keywords: ZnO Varistors, Composite Varistors, Polymers, Electrical Strength, Intensity, Modification, X-Ray Spectra.

1. INTRODUCTION

One of the promising areas of application composite materials is to use them as varistors, i.e., as non-linear element, the resistance of which depends on the applied voltage [1-5]. Finding the varistor effect in composites predetermined the existence of a potential barrier at the interface between semiconductors, ferroelectric piezoelectrics and polymers, the parameters of which depend on the strength of the electric field. Ease of manufacturing technology for composite varistors is that inorganic semiconductor or ferroelectric piezoelectric varistors mainly are made using ceramic and polymer technologies.

The problem of finding and developing a technology for obtaining new, more efficient composite dielectrics is associated with the complexity of the problems put forward by practice and technical application. Among them, composite materials based on thermoplastic polymers dispersed with varistor ceramic fillers are of great practical interest. These materials can have good varistor properties combined with good physical and mechanical properties. It should be noted that the idea of developing composite varistors is based on the model of the formation of the varistor effect in semiconductor ceramics. In composite varistors, a polymer matrix functions as an amorphous phase for ZnO or SiC ceramics; and as crystallites of ZnO or SiC - microscopic particles of ZnO or SiC. This combination of components contributes to the formation of a potential barrier at the polymer-semiconductor ceramic interface, and hence the varistor effect.

Mechanical and electrical strength the characteristics of active dielectrics are one of the most important performance indicators in any areas of their application. So, for example, passing shock wave along the varistors is accompanied by the occurrence the development of an electric field in them, which promotes accelerated destruction of the specified element.

Currently, there are mainly three directions in the field of creating varistor elements based on active solid dielectrics and semiconductors. One of them is associated with the creation of more and more semiconductor varistor materials [6, 7]. The second is based on the synthesis of new polymer dielectrics exhibiting varistor properties. The third direction is associated with the creation of various composites based on polymers (matrix) and inorganic semiconductors and ferroelectric piezoelectrics (dispersant). Establishing the relationship between the characteristics of composite varistors and the properties of the polymer phase and semiconductor fillers is undoubtedly a key issue on the way to solving this very important the problem of creating more efficient composite varistor elements for various purposes.

It is known that electrical equipment is often exposed to alternating polarized impulses. In this regard, at present, one of the main problems is the protection of microelectronics, electronic devices and their functional elements from switching and lightning voltages. Throughout the world, the electronics industry uses various types of varistors to protect electrical networks and electronic devices from all kinds of extreme electrical impulses. For this purpose, a ceramic varistor based on ZnO has found wide application, which differs from other materials in its superiority. It should be noted that one of the most promising areas for the development of protective devices and elements is the creation of two- and multiphase composite materials based on ZnO ceramic varistors. By synthesizing these composites based on ceramic phases and polymers, it is possible to obtain cheaper and higher-quality composite varistors, which can be used in low-voltage and high-voltage devices in the electric power industry.

The purpose of the work is to develop a technology for creating composite varistor elements with adjustable response voltage and to study the influence of electrical properties on composite varistors based on Zno-polymer.

2. METHOD OF ANALYSIS

Like all active and passive composites, the study of the electrical properties of polymer-based composite varistors is of particular importance. Determination of electric strength allows us to study the role of electron-ion processes and interfacial effects in the formation of varistor effects in composites. In addition, the determination of marked macroscopic parameters plays a huge role in optimizing the operation modes of composite polymer-based varistors.

In our case, to determine the electric strength of a composite varistor, it is first necessary to determine their breakdown voltage (which the sample is destroyed) and the opening voltage at this voltage, the sample passes a large current. Note that many models are used to explain the electrical breakdown of a dielectric [1, 2]. It is believed that electrons under the influence of a strong electric field, through the tunnel effect or under the influence of thermal ionization of impurities, leaving the electrode or impurity molecule fall into the conduction band. In the conducting zone, they accelerate and gain energy in order to tear new electrons from the forbidden zone. This process, by its nature, corresponds to a gas electric discharge in gases. In contrast to electron transfer in gases, electron transfer in solid dielectrics is associated with losses, since the motion of atoms in a solid dielectric causes a little scattering of electron energy.

Small molecular compounds in the bulk of solid dielectrics, such as impurities, make the structure of the dielectric unstable, and as a result, the additive centers become an electron energy scattering factor. When the energy of electrons entering the conductive zone exceeds the ionization energy, an electron flow is formed in the dielectrics. The flow of electrons in the dielectric releases energy and, as a result, the dielectric is locally destroyed. According to the mechanism of a pure "electric break", the electrical breakdown should not depend on the temperature of the electric strength $E(T)$. Experiments show that this mechanism can manifest itself in crystals with a sufficiently large conduction band [1, 2].

Taking into account all of the above problems, in our work, we studied the electrical properties of composites based on ZnO polymer. To establish the scope of the intended use of composite varistors, breakdown voltages and opening voltages were determined. In addition, the intensity value was determined after and before the modification of the composites in an electric gas discharge. And also, on the basis of X-ray spectra, a plot of the intensity values versus the percentage of filler at various Miller coefficients was constructed. An X-ray diffraction pattern was taken for the ZnO ceramic varistor.

It should be noted that it is important to determine the opening voltage and compare it with the breakdown voltage in composite varistors. It is also important to study the effect of ceramic and polymer phases on these parameters (U_{op} and U_{br}).

Figure 1 shows the dependence of the breakdown voltage on the percentage of filler of ZnO + PE composite varistors (polyethylene), and Figure 2 shows the dependence of the breakdown voltage on the percentage of filler of composite ZnO+F2M varistors (polyvinylidene fluoride).

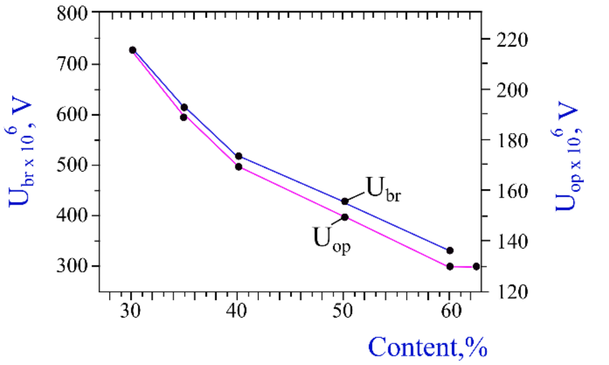

Figure 1. The dependence of the of breakdown (U_{br}) and opening voltages (U_{op}) on the percentage of the filler of the composite varistors based on ZnO-PE

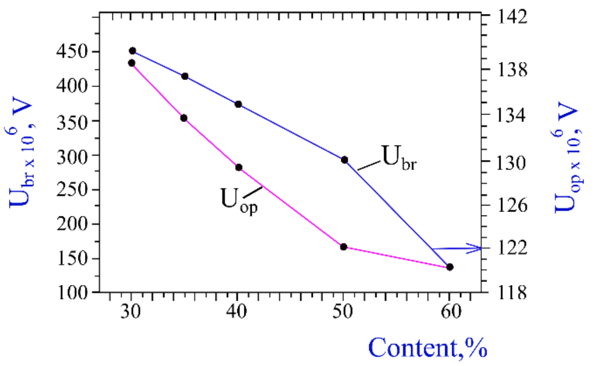

Figure 2. The dependence of the of breakdown (U_{br}) and opening voltages (U_{op}) on the percentage of the filler of the composite varistors based on ZnO-F2M

Figures 1 and 2 show the dependence of the quantity breakdown voltage (U_{br}) and voltage actuation (U_{op}) from the volumetric content of the inorganic phase (dispersant). It can be seen that for all values of the volumetric content of the dispersant, the value of U_{br} more than U_{op}. Similar results were obtained and for varistors based on ZnO-F2M. To explain some of the results on the formation of the varistor effect in highly heterogeneous materials ZnO-polymer consider the roles of charged particles and relaxation processes in the formation of electrical breakdown of the investigated varistors.

It is known that the initial stage of electron-ion processes in composites under the action of a strong the electric field is the injection of electrons into composite, stabilization of injected electrons on various traps of the polymer phase, charge transfer to the phase interface, and the formation of a potential barrier at the ZnO - polymer interface. Exactly presence of a potential barrier at the interface phases determines the mechanism of formation of the varistor effect in these systems. Therefore, according to our opinion, studies of the influence of relaxation phenomena of injected charged particles on the temperature the dependence of the electrical lifetime of composite materials is of interest from the point of view of creating low-power varistors for various purposes.

It should be noted that when discussing the results with an increase in the volume of the filler, it is necessary to take into account the decrease in the thickness of the polymer phase and the change in interfacial interaction. It should also be noted that as the filler percentage increases, the contact area of the polymer phase with ZnO ceramics also increases, and this leads to the formation of the molecular structure of composite varistors [4-10].

Before analyzing the results, we note that the main causes of electrical failure of composites are the following:
- the creation of effective (free) electrons, which form the basis of the process of electrical breakdown;
acceleration of effective electrons and, as a result of
- ionization processes inside dielectrics, the creation and transfer of new electrons;
- the formation of a local electric field inside dielectrics and the formation of a positive Streamer;
- superposition of the electric field applied by the local electric field, which is associated with the development of a positive Streamer;
- as a result of superposition, the creation of a strong electric field in the anode-cathode range and the intensity of ionization processes under its influence;
- creating a space charge inside the composite;
- the creation of new radicals as a result of breaking the polymer chain.
- the formation of thermal effects as a result of an increase in the value of the current flowing through the discharge channel;
- the destruction of the dielectric, that is, the composite, under the influence of heat and electricity at the same time. If the amount of heat generated by the electric field applied to the dielectric is greater than the heat supplied to the environment as a result of heat exchange, the dielectric strength and current increase with increasing dielectric temperature, causing the destruction of the sample [3].

Dielectric breakdown occurs due to rapidly developing electrical phenomena, mainly due to ionization of electrons and significant changes associated with the heterogeneity of the dielectric. Therefore, the electric discharge is less dependent on temperature, sample thickness, and electric field duration. For a discussion of the results should consider the following:
- a decrease in the thickness between the particles of the polymer phase with an increase in the percentage of filler;

- change in interfacial interaction;
increase the area of contact of the polymer phase with ZnO ceramics;
- the role of reducing the volumetric content of the filler in the formation of the molecular structure of the polymer phase [4-11].

Let us compare the change in the breakdown voltage of composites depending on their polymer matrix. The results show that the ratio U_{br}(PE)/U_{br}(F2M) is almost two times different from the total filler percentage. If we assume that in all percentages obtained, the thickness of the polymer phase in the filler-PE and filler-F2M composites is the same and the surface of the filler particles affects the molecular structure of this layer, then we can say that the ratio of the breakdown voltage of the composites obtained on the basis of F2M and PE will be equal to the ratio of the breakdown voltage of a pure polymer sample based on F2M and PE. The electric strengths of the polymers PE and F2M used by us are 40 kV/mm and 25 kV/mm, respectively. The electric strength ratio of PE and F2M is 1.6 kV/mm. This shows that the process of electrical scattering in both polymer composites is largely dependent on the interaction of particles or the electro physical properties of the transition phase. The results are shown in Table 1.

Table 1. Electrical strength of composites

Composites	E_{stren}, V/m		
	PE	F2M	Relativity
100% polymer	40×10^6	25×10^6	1.6×10^6
10%C+90% polymer	13.04×10^6	6.65×10^6	1.96×10^6
30%C+70% polymer	3.085×10^6	2.047×10^6	1.507×10^6
50%C+50% polymer	1.103×10^6	0.64×10^6	1.72×10^6
60%C+40% polymer	0.904×10^6	0.456×10^6	1.98×10^6

The results obtained (Table 1) show that the role of intermolecular chemical interactions in the studied composite varistors is small. Indeed, if the chemical interactions at the interface were serious, then the macroscopic characteristics of the varistors we studied would be less stable.

It was shown in [11] that relaxation phenomena in composites are the main factor in the emptying of traps and, consequently, the appearance of free electrons, which determine the onset of electrical breakdown of the heterogeneous ZnO - polymer system. If take into account that the development of relaxation phenomena is closely is related to temperature, then the study of temperature time dependence of the lifetime of the varistor material will reveal the role of injected charged particles and relaxation processes of the composite.

Figure 3a shows the dependence of the electric lifetime on temperature. Observed maxima at 175 and 250 K. Such a change in $\log\tau E$ from temperatures can be explained as follows.

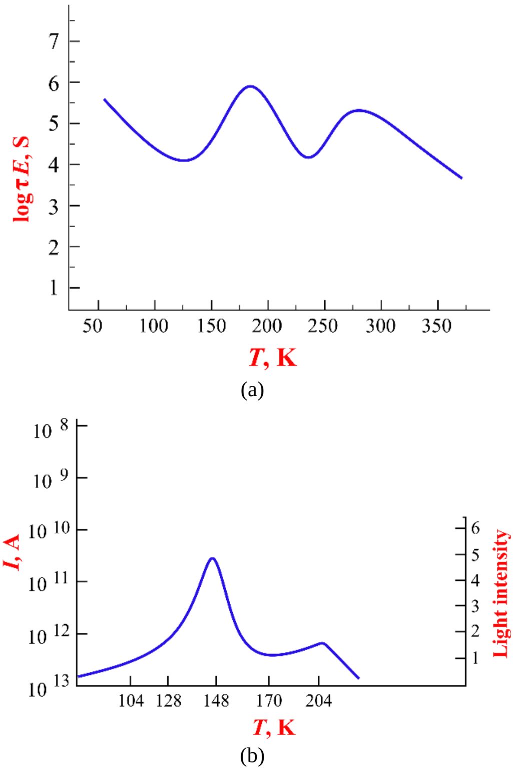

Figure 3. a- dependence of the logarithm of the polyethylene lifetime on temperature, b- spectrum of thermally stimulated depolarization current of the polymer - ZnO composite [11]

- comparison of the temperature dependence of the lifetime with the thermally stimulated depolarization current (*TSD*) of the polymer (Figure 3b);
- determination of the sources of education of free effective electrons, which are the beginning the process of electrical destruction.

According to Artbauer's theory [11], the presence of gas inclusions in polymers larger than 50 A° leads to the occurrence of partial discharges, which rye are ultimately accompanied by destruction (breakdown) of polymers in a strong electric field. Taking this into account, we assume that in a heterogeneous system polymer-ZnO, gas inclusions of various sizes. It is these foci in strong electric fields are the main cause of electrical destruction of polymer - ZnO varistor composites. This effect is confirmed by the coincidence of the TSD maxima and the dependence $\log \tau E = f(T)$ (Figure 3b).

The regulation of microscopic physical structure of the PE-ZnO system will make it possible to create composite varistors with a high electric breakdown field strength in comparison with its voltage triggering.

The discharge of electric gas can change the chemical structure of the polymer [3]. To analyze the results obtained, composite varistors are modified at a voltage of 3 kV for 3 minutes during an electric gas discharge.

Note that after an electric discharge, the degree of crystallization of the composite can increase or decrease. The reason for the increase in the degree of crystallization of the composites is that the amorphous phase of the polymer is destroyed faster than the crystalline phase (Figures 4, 5 and 6).

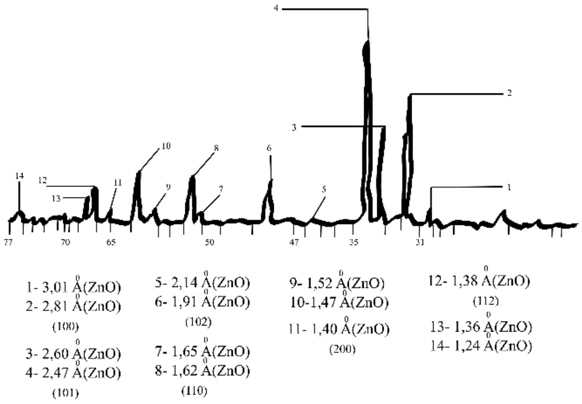

Figure 4. Diffractogram of the ZnO

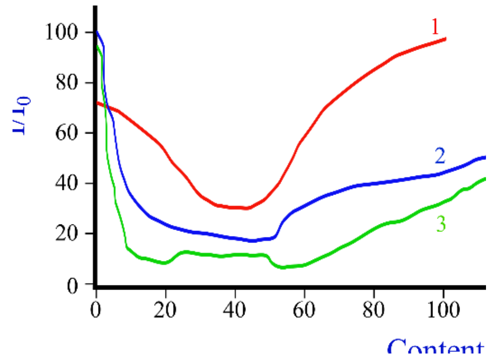

Figure 5. Diffractogram of the intensity value for the various Miller coefficients by the percentage of the filler volume 1-(101), 2-(110), 3-(002)

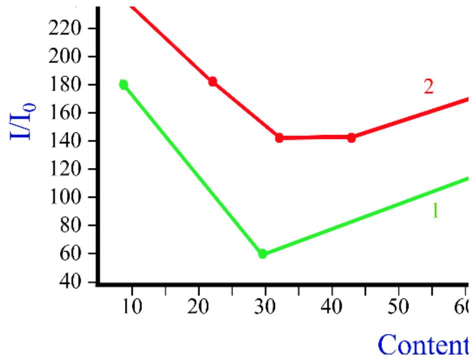

Figure 6. The dependence of the intensity value on the percentage of the filler of the composite varistors based on ZnO-F2M

1 - unchanged sample of electric gas discharge;
2- 3 minutes modified version of electric gas discharge

To consider changes in the crystallization degree of the modified composites, X-ray spectra were recorded. As a result of the experiment, it was found that the crystallization of composites increases after the process of electric discharge.

In Figure 4, specific reflections are observed, which belong to ZnO used as fillers in composites. In Figure 5, a diffraction pattern was constructed for different Miller coefficients depending on the intensity value on the percentage of filler. Note that the dependence of the intensity on X-ray spectra on the percentage of filler is the same, regardless of different Miller coefficients [5-11].

Figure 6 shows after modification of the composites for 3 minutes in an electric gas discharge, their intensity increases.

3. CONCLUSIONS

In our work, we discuss the development of a technology for creating composite varistor elements with adjustable response voltage and study the effect of electrical properties on composite varistors based on ZnO polymer. It turned out that the breakdown voltage and the opening voltage are the same. It was determined that the sources of formation of free effective electrons are the beginning the process of electrical destruction. It was also found that for various Miller coefficients, the dependence of the intensity value on the volume of the filler is of the same nature. After modification of the composites for 3 minutes in an electric gas discharge, their intensity increases. It is important to note that the determination of all these parameters is important for the correct clarification of the field of application of composite varistors.

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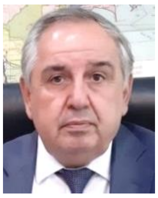
BIOGRAPHIES

Shafag Mirbaba Ahadzadeh was born in Shirvan, Azerbaijan on February 16, 1979. She graduated from Electrical Engineering Department of Azerbaijan Technical University (Baku, Azerbaijan) with a diploma of distinction in 2002. She began her scientific work at the Institute of Physics, Azerbaijan National Academy of Sciences (Baku, Azerbaijan) as an engineer in the laboratory of "Physics and High Voltage Engineering" in the group of composite material. In a short time, she mastered both practical and theoretical skills of this specialty. In 2010, she successfully defended her thesis on the topic "Varistor effect of composite materials based on polymer and zinc oxide ceramic with various impurities". She has participated in a number of national and international scientific conferences, published about 35 scientific articles, and has 2 patents. She is a leading researcher. Currently, she is studying on the mechanism of the formation of the varistor effect in composites based on polar and nonpolar polymers and zinc oxide ceramics with various impurities.



Arif Mamed Hashimov was born in Shahbuz, Nakhchivan, Azerbaijan on September 28, 1949. He is a Professor of Power Engineering (1993); Chief Editor of Scientific Journal of "Power Engineering Problems" from 2000; Director of Institute of Physics of Azerbaijan National Academy of Sciences (Baku, Azerbaijan) from 2002 up to 2009; and Academician and the First Vice-President of Azerbaijan National Academy of Sciences from 2007 up to 2013. He is laureate of Azerbaijan State Prize (1978); Honored Scientist of Azerbaijan (2005); Cochairman of International Conferences on "Technical and Physical Problems of Power Engineering" (ICTPE) and Editor in Chief of International Journal on "Technical and Physical Problems of Engineering" (IJTPE). Now he is a High Consultant in "Azerenerji" JSC, Baku, Azerbaijan. His research areas are theory of non-linear electrical Networks with distributed parameters, neutral earthing and ferroresonant processes, alternative energy sources, high voltage physics and techniques, electrical physics. His publications are 280 articles and patents and 5 monographs.

Shahla Ganbar Khalilova was born in Azerbaijan on November 18, 1977. She received the B.Sc. in Physics from Baku State University, Baku, Azerbaijan in 2005, and the M.Sc. degree in Heat physics and molecular physics from the same university. She is with Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan as Scientific Researches (2006) and as Postgraduate Student (2011-2015). Her research interests are in development theoretical foundations of electrophysical methods used in technological processes. Investigation of electrical properties of composite materials based on polymer dielectrics.