

Electrophysical Characteristics of Composite Nonlinear Resistors Based on Polymer and Bentonite

Sh. M. Gasanli^{a,*}, S. R. Imanova^b, and U. F. Samedova^a

^a *Institute of Physics, Azerbaijan National Academy of Science, Baku, AZ-1143 Azerbaijan*

^b *Gandzha State University, Gandzha, AZ-2000 Azerbaijan*

**e-mail: hasanli_sh@rambler.ru*

Received February 1, 2017; in final form, March 23, 2017

Abstract—The current–voltage characteristics and the resistivity of composite resistors (varistors) based on a non-polar polyethylene and bentonite (a clay mineral) were investigated. It was found that the content of composite components influences to the current–voltage characteristics and the magnitude of resistivity. It was shown that when increasing the molar content of the filler, the magnitude of resistivity decreases exponentially.

Keywords: polymer, bentonite, composite, montmorillonite, nanocomposite, conductivity, resistivity

DOI: 10.3103/S1068375518030031

INTRODUCTION

The development and research of properties of layered-silicate polymer nanocomposites are a promising line of polymer chemistry due to the ability to produce the nanostructured materials with improved performance properties. At the end of the 1980s, researchers of the Toyota concern produced the first nanocomposite based on polyamide-6 and organomodified montmorillonite, which revealed increased physical-mechanical and thermal properties that determined the prospects of such systems and the surge in investigations in this field [1–5]. To date, the market of layered-silicate polymer nanocomposites is one of the most dynamically developing markets with a volume of about 950 million dollars. Let us note that the production of polymeric compositions with special electrophysical properties depends largely on the nature of filler, of the form, size, and pattern of particle distribution, as well as on the degree of interaction between the components. The nature of filler particle aggregation, crystallization conditions and a number of other factors change the morphology of polymer matrix and, as a result, the composite materials produced on this basis obtain unique properties, which leads to increasing possibilities of their practical application. In contrast to traditional nonlinear devices, this is due to their containing symmetrical current–voltage characteristics (CVC). The development of physical chemistry and technology of composite materials, which in most cases are filled with linear and cross-linked polymers, requires refinement of our concepts of the pattern of their short-range ordering and on their supra-molecular order. In addition, the contact phenomena, and changes in the electrophysical and electroactive

properties of heterogeneous systems of the polymer-filler type, especially of interphase phenomena, have been little studied.

Let us note that the field of application of composite materials extends from nanoelectronics and integrated microcircuits to low-power dischargers (switching elements) of different purposes [6, 7].

The work is devoted to studying the influence of the volume content of filler to the CVC and magnitude of resistivity (under a fixed voltage) of composite nonlinear resistors based on nonpolar polymer—polyethylene (PE) and bentonite (clay mineral)—montmorillonite.

The bentonite of the Das-Salahli field is used in the work. This bentonite is referred to as the type Namontmorillonite. The percentage of montmorillonite in the bentonite clays, which are mined in the Das-Salahli field, is from 80 to 95%. This field is one of the high-quality natural sodium deposits. It is seen from Table 1 that the chemical composition and percentage of chemical compounds of this bentonite is in a good agreement with the data of bentonites from other fields [8, 9].

Montmorillonite is one of the rock-forming minerals of bentonite clays, fields of which are located all over the world and refers to the clay minerals from the group of smectites of a subclass of layered silicates. The chemical composition is changeable and strongly depends on the variable water content. The following fluctuations (in %) are stated according to the analyses of the net differences: SiO₂, 48–56; Al₂O₃, 11–22; Fe₂O₃, 5 and further, MgO, 4–9; CaO, 0.8–3.5 and H₂O, 12–24. In addition, sometimes K₂O, Na₂O and

others are identified. They have a monoclinic crystal system and layer crystal structure. The polar liquids (glycerin), exchangeable cations and anions sometimes enter into the interlaminar space. Their color is white, grayish-white, bluish, pink, reddish-pink, and greenish. The energy gap width is 3.7 eV [10]. Many bentonite clays consisting of montmorillonite were formed as a product of decomposition of volcanic ashes, deposited mainly in the marine basins. Owing to the high absorption capacity, the montmorillonite clays are widely used for various purposes in industry, including petroleum, textiles and cosmetics, medicine, etc., either directly in the dried form, or after preliminary chemical treatment (activation). The choice of polyethylene (PE) as a binding material is a result of detailed study of its electrophysical properties. Choosing bentonite is related to poor knowledge of its electrophysical characteristics, as well as with its availability for production of new sufficiently flexible thin film composites with new properties.

EXPERIMENTAL TECHNIQUE

Bentonite-montmorillonite and low-pressure polyethylene in the form of powders were used as the components. To produce the composites, the powders of bentonite (BT) and polymer were previously shredded in a ball mill with porcelain balls to a granule size of less than 5 μm . The composites were produced from a homogeneous mixture of components by hot pressing at a temperature of 140°C and a pressure of 15 MPa. The contents of composites was varied over a wide range of components (5–70% of BT and 95–30% of PE, respectively). The thickness of specimens was on average 150 μm . Silver paste was used as an electrode material. The dependences of CVCs and resistivity on the volume content of filler (BT), as well as the dielectric properties of all specimens were investigated.

The parameters of the studied specimens were measured at room temperature. The experimental results are represented in Figs. 1–6.

The photomicrography of composite structure shows that the filler particles in a composite are distributed sufficiently heterogeneously, namely, the neighboring filler particles are separated with a layer polymer of a matrix (Fig. 1). The photomicrography of a composite was obtained using an Altami model microscope.

The diffraction patterns of unannealed and annealed ($T_{\text{ann}} = 200^\circ\text{C}$) bentonite powders were obtained with a XRD D8 model diffractometer (Broker Company) with $\text{CuK}\alpha$ radiation (Fig. 2a). Figure 2a presents the diffraction pattern of annealed ($T_{\text{ann}} = 200^\circ\text{C}$) bentonite powder, at which the characteristic peak in the area of $2\theta = 7.5^\circ$ is clearly visible, which corresponds to the Bragg period of locations of heterogeneous regions and responsible for the distance between the basal surfaces of a clay.

Table 1. Chemical composition of Das- Salahli bentonite

Chemical compounds	Quantity, %	Chemical compounds	Quantity, %
SiO_2	58.60	MgO	2.30
Al_2O_3	13.40	P_2O_5	0.11
Fe_2O_3	4.70	SO_3	0.25
FeO	0.18	K_2O	0.39
TiO_2	0.39	Na_2O	2.30
CaO	2.05	poi*	15.33
Sum total			100

*poi—percentage of other impurities.

Moreover, the multiphase nature of the initial material is seen in the diffraction pattern, namely NaAl , Si - et al. ($2\theta = 6^\circ, 20^\circ, 35^\circ, 54^\circ, 62^\circ$) reflexes, as well as Albite , syn ($2\theta = 28^\circ$) reflexes are noticeable. It is seen also in Fig. 2a that despite the annealing, the diffraction pattern of the powder has an amorphous behavior, in other words, the degree of crystallinity of the initial powder is low (further annealings lead to the growth of crystallinity of the powder. A separate article will be devoted to this subject). The analysis of the IR spectrum shown in Fig. 2b revealed the presence of various structural groups in bentonite, namely, the valence oscillations of OH -groups in the range of 3400–3600, the valence oscillations of Si-O-Si and Si-O-Al when 1037, the deformation oscillations of H_2O when 1635 and Al-OH-Mg when 843, etc. Let us note that the data of the IR spectrum are in a good agreement with the data presented in [11, 12].

It is seen in Figs. 3a and 3b that the dependence of the magnitude of the current (CVC) on the applied voltage at the studied composites has a nonlinear

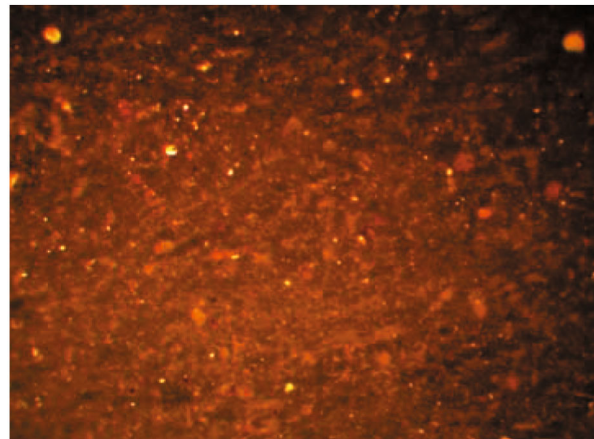


Fig. 1. Morphology of composite surface.

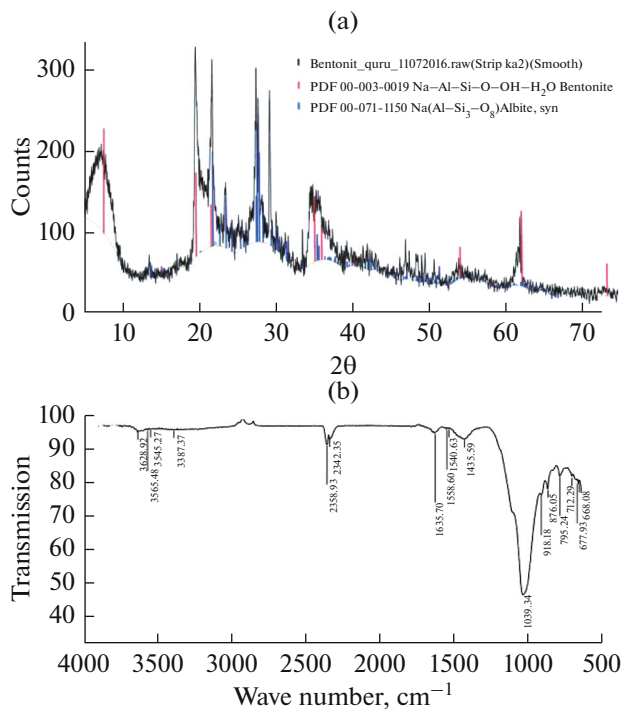


Fig. 2. (a) X-ray of annealed (200°C) initial bentonite. (b) IR spectrum of bentonite.

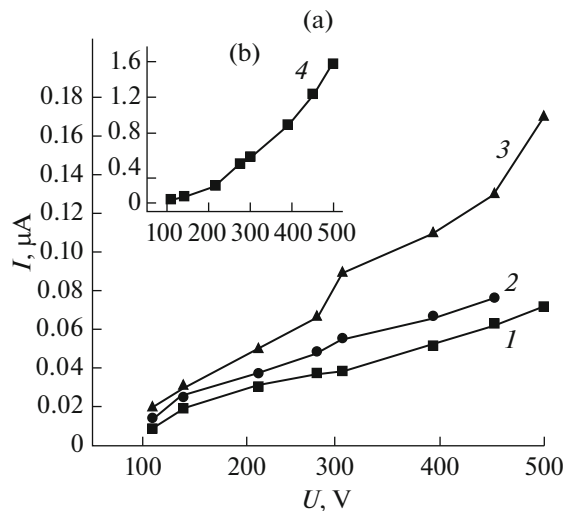


Fig. 3. Current–voltage characteristics of composites with various filler content: (a) (1) BT 5% + PE 95%; (2) BT 10% + PE 90%; (3) BT 20% + PE 80%; (b) (4) BT 30% + PE 70%.

behavior (the nonlinearity of CVC is pronounced when BT > 30%). Thus, the magnitude of current through the composite increases and changes by 1–2 orders of magnitude, i.e., the CVC has a varistor behavior. It is seen in Fig. 4 that the CVC of pure bentonite is also

nonlinear. In this regard, let us note some distinctive features of the CVC of composite and pure bentonite:

(1) Unlike the composite, the nonlinearity of CVC in bentonite is observed in the region of low values of applied voltage (Fig. 4) which strongly limits their practical application.

(2) The large magnitude of electrical conductivity in the initial bentonite to a great extent depends on the weakly-bound ions of oxides of alkali metals (Na_2O , K_2O) under the influence of thermal motion can break away from the bedding points and move from one cell of the spatial grid to another cell. Thus, the ion-relaxation polarization intensifies, as a result, the number of ions, which are involved in the electrical conductivity process, increases. In addition, the smaller the ion radius, the larger its mobility and contribution to electrical conductivity. Since the radius of the sodium ion is smaller than the radius of potassium ion, respectively, it will influence the electrical conductivity of bentonite more. The presence of water molecules in bentonite is also a strong influence on its electrophysical properties.

At the same time, by variation in the percentage of components, the composite makes it possible to synthesize thin film high-resistance resistors with different varistor voltages (varistor opening voltages), as well as with dielectric parameters (in particular, with dielectric permittivity exceeding 1000), which can be applied in various fields of microelectronics and electrical engineering.

Numerous experimental results reveal that the generation of the varistor effect in composites is directly related to the presence of a potential barrier at the borders of the filler, an amorphous phase [6, 7].

Based on the experiments for all composites, the resistivity was calculated. Figure 5 shows the dependence of resistivity (when $U = 100, 300 \text{ V}$) on the percentage of filler (BT), which can be conditionally partitioned into two sections (1) and (2). As seen in Fig. 5, despite the different values of applied voltage, the dependence of resistivity on the percentage of filler is exponential. In the initial section (1) the resistivity ρ is large and mainly determined by the resistance of the polymer. With an increase in the percentage of filler, ρ exponentially decreases (section (2)) with a constant output when the filler content (BT 30–32%).

DISCUSSION OF EXPERIMENTAL RESULTS

According to [13, 14], the conductivity of composition is a function of the average number of contacts per one particle. In addition, according to the theory of electrical contacts, the current between two conductors can flow not only in direct contact, but if there is a thin layer of dielectric between them. In that case, the conductivity can be achieved by the tunneling of charge carriers through potential barriers [13]. In turn,

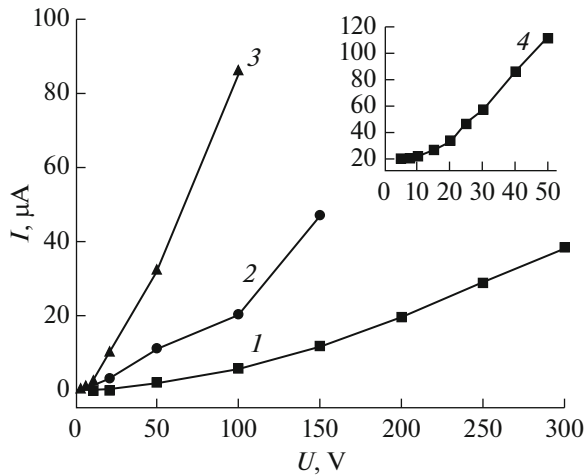


Fig. 4. Current–voltage characteristics of composites with various filler content: (1) BT 50% + PE 50%; (2) BT 55% + PE 45%; (3) BT 70% + PE 30%; (4) BT 100%.

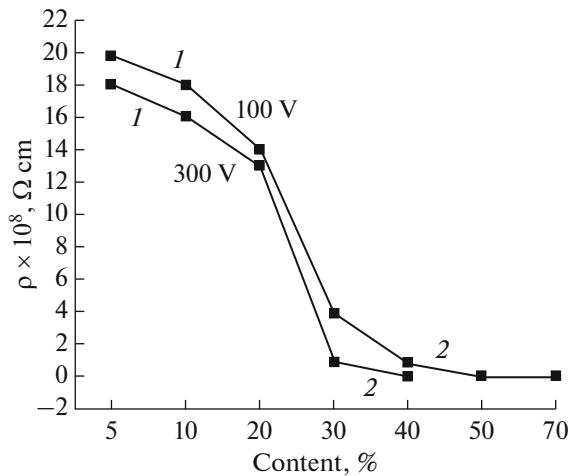


Fig. 5. Dependence of electrical resistance of composite on the percentage of filler (when 100 V and 300 V).

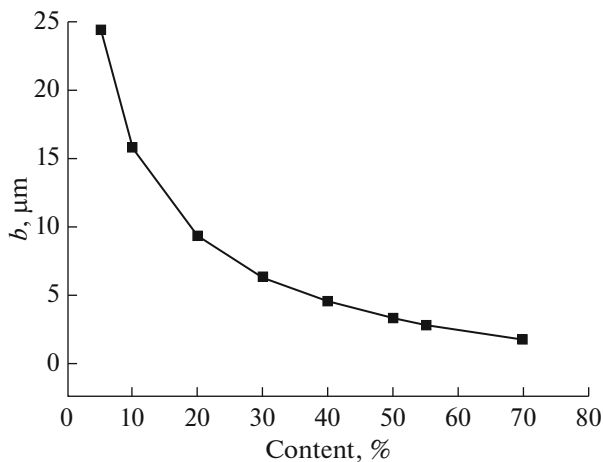


Fig. 6. Dependence of the distance between the filler particles on their percentage.

according to [7, 13], the potential barrier height at the phase interface is defined by following formula:

$$\varphi = \frac{e^2 n_d b^2}{2\epsilon_k \epsilon_0}, \quad (1)$$

where e is the electron charge; n_d is the concentration of donors; b is the width of polymeric layer between neighboring particles of the filler; and ϵ is the dielectric permittivity of the composite.

According to [15], the distance between the filler particles in the polymer (the thickness of polymer layer) can be calculated by the formula:

$$b = d \left(\left(\frac{\pi(1+C)}{6C} \right)^{1/3} - 1 \right), \quad (2)$$

where C is the filler volume fraction in the polymer; and d is the diameter of filler particles.

The results of calculations are shown in Fig. 6, from which it is seen that the dependence of b on the filler volume fraction (C) has an exponential behavior.

Taking into account formulas (1) and (2), it appears that the dependence of resistivity on the volume fraction of BT filler (Fig. 5) can be explained as follows: when there is a low content of filler owing to the large thickness of polymer layers between the filler particles (see Fig. 5), the magnitude of the potential barrier is large (I). In turn, due to the exponential dependence of the tunneling resistance

$$R \sim \exp(\varphi/kT) \quad (3)$$

on the potential barrier, the probability of tunneling of charge carriers through a thick barrier is small, and the contribution of tunneling conductance will be insignificant (Fig. 5, region 1). Therefore, the resistance of the composite will be mainly defined by the polymer resistance. The conductivity at this section is mainly a stick-slip behavior. When further increasing the percentage of filler, the thickness of the polymer layers between filler particles decreases (see Fig. 6), and thus the average number of contacts between the particles increases. As a consequence, the magnitude of potential barrier φ and tunneling resistance R (3) decrease. As a result, the conductivity increases and correspondingly the composite resistivity decreases (Fig. 5, region 2). When further increasing the filler content, the filler particles begin to form continuous chains, and, therefore, the conductivity of the composite will mainly be determined by the conductivity of the filler particles. In fact, as seen in Fig. 5, when the filler percentage exceeds 32%, the resistivity tends to a constant value.

CONCLUSIONS

The results allow us to draw the conclusion on the prospects of composites, which are a highly concentrated system of macro-nanoparticles based on a non-polar polymer polyethylene (PE) and bentonite (clay

mineral), montmorillonite, which in the future will make it possible to develop various low-voltage, low energy consuming, cheap varistor elements, as well as other components for use in microelectronics and other fields of electrical engineering.

REFERENCES

1. Damião Leitea, A.M., Araujo, E.M.R., and da Paza, A., *Mater. Res.*, 2009, vol. 12, no. 2, pp. 165–168.
2. Beyer, G., Henrist, C., Cloots, R., Rulmont, A., Jérôme, R., and Duboi, P., *Macromol. Rapid Commun.*, 2001, vol. 22, no. 8, pp. 643–646.
3. Gerasin, V.A., Bakhov, F.N., Merekalova, N.D., Korolev, Yu.M., Zubova, T.L., and Antipov, E.M., *J. Eng. Phys. Thermophys.*, 2005, vol. 78, no. 5, pp. 871–877.
4. Chvalun, S.N., Novokshokova, L.A., Korobko, A.P., and Brevnov, P.N., *Ross. Khim. Zh.*, 2008, vol. 3, no. 5, pp. 52–57.
5. Fischer, H.R., Gielgens, L.H., and Koster, T.P.M., *Acta Polym.*, 1999, vol. 50, no. 4, pp. 122–126.
6. Souza, F.L., Gomes, J.W., Bueno, P.R., et al., *Mater. Chem. Phys.*, 2003, vol. 80, p. 512.
7. Valeev, Kh.S. and Kvaskov, V.B., *Nelineinye metallooksidnye poluprovodniki* (Nonlinear Metal Oxide Semiconductors), Moscow: Energoizdat, 1983.
8. He, M.-C., Fang, Z.-J., and Zhang, P., *Chin. Phys. B*, 2009, vol. 18, pp. 2933–2937.
9. Kukovskii, E.G., *Osobennosti stroeniya i fiziko-khimicheskie svoistva glinistykh materialov* (Specific Structure and Physical-Chemical Properties of Clay Minerals), Moscow: Khimiya, 1966.
10. Gorbunov, N.I., *Vysokodispersnye mineraly i metody ikh izucheniya* (Fine Minerals and Their Analysis), Moscow: Goskhimizdat, 1963.
11. Rakitskaya, T.L., Knose, T.A., Dzhiga, A.M., and Toporov, S.V., *Mezhd. Nauch. Vestn.*, 2012, vol. 12, no. 51 (41), pp. 13–17.
12. Tolstenko, D.P. and Vyatkina, O.V., *Uch. Zap. Tavrich. Nats. Univ. im. V.I. Vernadskogo, Ser. Biol., Khim.*, 2011, vol. 24, no. 3, pp. 185–191.
13. Kjstic, P., Milosevic, O., and Pistic, M.M., *Physica B + C* (Amsterdam), 1990, vol. 150, nos. 1–2, p. 175.
14. Aharoni, S.M., *J. Appl. Phys.*, 1972, vol. 43, no. 5, p. 2463.
15. Losoto, L.P., Usichenko, V.M., Budnitskii, Yu.M., et al., *Dokl. Akad. Nauk SSSR*, 1984, vol. 27, no. 6, p. 1410.

Translated by M. Kromin