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MAGNETIC AND ELECTRICAL PROPERTIES OF COMPOSITES BASED ON BENTONITE AND POLYETHYLENE MODIFIED WITH MAGNETIC PARTICLES

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Field of science: Physics

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

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The work was performed at the Institute of Physics of the Azerbaijan National Academy of Science in the Laboratory 1.8 "High voltages physics and technology".

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GENERAL CHARACTERISTICS OF THE WORK

Relevance and degree of elaboration of the topic. Creation of devices operating at high-frequency electromagnetic fields, high temperatures, enhanced radiation, etc., is among the key fields in semiconductor electronics. Over the last years, studies covering the processes of obtaining composites based on polymers and natural layered silicates have been extensively developing. Polymer composites have a number of distinctive properties. As a result, they are widely used in microelectronics, information systems, etc. Interactions at the interphase boundaries lead to a change in the properties of specific components of the systems as a whole. As a result, composites acquire fundamentally new properties. This in turn leads to an increase in the possibilities of their real-world application. Quite the same way, bentonite composites modified with magnetic nanoscale particles can be in widespread use in various fields of electric and radio engineering as semiconductor and dielectric materials to create sensors of electric and magnetic fields of chokes, transformer and antenna cores, as well as radar-absorbent materials. The dispersion of Fe_2O_3 ferrites allows us to consider these substances as effective sorbents. The structure and distribution of Fe_2O_3 ferrite nanoparticles can originate under the influence of an external magnetic field. Electrical resistance ρ is among the most important electrophysical properties for each material used for the production of various electronic devices. It determines the electrical conductivity of a given material. This makes it possible to apply the percolation model considered within many studies to describe the electric and magnetic properties of an inhomogeneous medium. The application of percolation theory helps to create a particle distribution for the resulting properties of the sample to solve the tasks. At the same time, identifying the percolation threshold parameters, the electric and magnetic properties are limited to a certain area of the percolated medium. The geometric features of the fractal set letting the percolation to take place near the percolation threshold are determined by the laws of criticality.

The features of nanocomposite media have significant differences from the parameters of individual nanoparticles being part of composites. Many nanoclusters form a nanocomposite medium with effective dielectric and magnetic permeabilities. These nanostructures are called an effective medium model and are essential to the physics of nanocomposites.

Taking into account their advantages mentioned above, the study of the electrophysical and magnetic properties of composite magnetic materials and the construction of cores based on them, as well as sensors of ultrahigh frequency and power magnetic fields is relevant. Their response speed is one of the most important parameters, mainly defined by the speed of relaxation processes. Thus, it is important to study the mechanisms of polarization and temperature dependences of polarization processes in the studied materials. Temperature studies of relaxation processes in bentonite nanocomposites with Fe_2O_3 ferrite filler at high frequencies and temperatures are insufficient. For this reason, we consider the study of the electric and magnetic properties of composite magnetic materials at high frequencies and in a wide temperature range as relevant.

All of the above circumstances stipulated the relevance of the subject of this dissertation.

Object of the research:. To establish the relationship between the regularities of current carrier transfer processes and to study the dielectric, electrophysical, and magnetic properties of bentonite composites with a polymer matrix and Fe_2O_3 ferrite filler in an external oscillating electric and magnetic field depending on temperature, frequency, in order to create elements of nanoelectronics, energy engineering, electric and radio engineering, etc. based on them.

The following issues have been resolved to achieve the goal indicated in the dissertation:

✓ Review and analysis of the literature covering this topic and bentonite.

✓ Selection of technology and establishment of production modes for thin-film bentonite- and polyethylene-based composites, as well as bentonite samples with ferrite (Fe_2O_3) filler.

✓ Studies of frequency and temperature dependences in the temperature range (300-600)K of dielectric and electrophysical properties of composites with a composition of (5-75)% bentonite and (95-25)% polyethylene.

✓ Creation of a percolation model of the produced bentonite composites and determination of their percolation parameters.

✓ Studies of the effect of particle size of the bentonite composite components on their dielectric, electrophysical and magnetic properties.

✓ Study of dielectric, electrophysical and magnetic properties of bentonite-ferrite (Fe_2O_3) composites in an external electric and magnetic field in the temperature range of (77-500)K and electrical conductivity in the range of (300-600)K.

Methods and target of research. Bentonite composites with a polymer matrix and composites with Fe_2O_3 ferrite filler were the target of the dissertation research. All studies were carried out using advanced experimental devices with high measuring accuracy. The studies were carried out for a pure bentonite sample with a thickness of 6.5 mm, composites with a thickness of 150 µm - 180 µm, the percentage of which varied in the range of 5-70% (BT) and 95%-30% (PE), as well as for cylindrical bentonite samples with Fe_2O_3 with a length of 16 mm and a diameter of 7 mm. Micrographs of composite surfaces were taken using an ALTAMI microscope. Diffractograms of bentonite powders were obtained by means of a *Broker* XRD-D8 diffractometer with CuK_α radiation. Measurements of capacitance C, resistances R and Z, and dielectric losses D of composites were carried out using a digital immitance meter, based on which the dielectric parameters **ε, tgδ, ε'', ε'**, and electrical conductivity **σ** of bentonite samples were calculated.

The main scientific provisions submitted for defense:

- The pronounced dispersion of dielectric parameters in the low-frequency region of the electric field, in the bentonite composites with polymer matrix of different composition, is explained by the Maxwell–Wagner polarization mechanism.

- The change in the resistivity value of bentonite composites is a result of changes in the bentonite content.
- Bentonite samples of different composition with a polymer matrix are sensitive to frequency and temperature changes.
- The percolation model defines the magnetic, electrical and dielectric properties of bentonite-ferrite Fe_2O_3 composites of different composition. Their electrical properties are described by the Efros–Shklovskii model.
- The conduction mechanism in bentonite-ferrite (Fe_2O_3) composites has a zonal nature. In the composites with 50% Fe_2O_3 (M_1) + 50% BT and 60% Fe_2O_3 (M_2) + 40% BT at a temperature of (300-500) K, dependence $\ln\sigma = f\left(\frac{10^3}{T}\right)$ indicates a semiconductor nature.
- The phase transition of magnetic samples with a composition of 50% BT + 50% Fe_2O_3 (M1) and 40% BT + 60% Fe_2O_3 (M_2) is observed at a temperature of (320-340) K, the so-called Curie temperature, with magnetic samples passing into paramagnetism states.
- The reduction in the size of Fe_2O_3 ferrite particles and bentonite particles affects the dielectric, electrophysical and magnetic properties of bentonite-ferrite composites.
- Detection of NMR (negative magnetoresistance) in bentonite-ferrite composites, changing with the increase in the size of ferrite particles.

Scientific innovation of the research:

- The regularities of dispersion of the dielectric parameters of bentonite composites in the frequency range (25-10^6) Hz of an oscillating electric field were studied.
- The electrophysical and magnetic properties of bentonite composites were explained within the percolation model with reference to the Efros–Shklovskii theory.

- The electrophysical characteristics of composites based on polyethylene (PE) and bentonite (BT), and the effect of the volumetric content of the filler on VAC (volt-ampere characteristics) and on the resistivity value (at a fixed voltage) were studied.
- The effect of the annealing temperature on the electrophysical and dielectric properties of bentonite samples annealed at a temperature of 400°C, 500°C, 600°C, 800°C, and 1000°C was studied.
- Temperature dependences of dielectric and electrophysical parameters of composites were studied. Temperature hysteresis was detected in the dependences of dielectric parameters of the composites with 30% (BT) + 70% PE and 50% (BT) + 50% PE.
- Frequency and temperature dependences of dielectric, electrophysical and magnetic parameters of bentonite composites on oscillating electric and magnetic fields were studied.
- The effect of the size of Fe_2O_3 magnetic particles on the value of the NMR in the studied bentonite samples, as well as the decrease of NMR with the increase of the oscillating magnetic field were studied.

Theoretical and practical significance of the research: The conducted study allowed us to get information about the conduction mechanism of current carriers, the dielectric parameters, the magnetic properties of composites, the effect of various factors on the electrophysical dielectric and magnetic properties in the studied composites. Bentonite composites with polymer matrix and Fe_2O_3 ferrite filler can be profitably employed in microelectronics, electric and radio engineering, etc. It will be possible to manufacture low-voltage, low-energy, cheap, varistor, as well as other elements based on the obtained composite materials. It can be used as an electronic frequency converter in the region of a drastic fall in resistance at (150-160) kHz, and as an excess-voltage suppressor during an increase in resistance at ($f > 160$ kHz). In this case, at low frequency values, the resistance does not interfere with the flow of current, and at high values of *f*, it will serve as an absorbing filter.

Bentonite-ferrite Fe_2O_3 samples with high values of $\boldsymbol{\mu}$ and low losses in the low frequency region can be used for radio components of high-frequency equipment, to create transformer antenna cores, chokes, etc. Samples with low values of μ in the high frequency region are efficiently used in the creation of radar-absorbent materials. The linear dependence of the intensity of magnetism of the bentonite-ferrite composites is common to magnetic dielectrics, widely used as cores in oscillatory circuits in electric and radio engineering. Elements with NMR based on bentonite and Fe_2O_3 can be used as electromagnetic wave absorbers.

Approbation and application. The dissertation materials were reported and discussed during the following conferences, meetings and seminars:

- Gənc alimlərin II beynəlxalq elmi konfransı. // Effect of modification on magnetic properties of composites based on magnetic particles and bentonite. (Gəncə Dövlət Universiteti 2017).
- Respublika Beynəlxalq Elmi Konfras Müasir təbiət Elmlərinin Aktual Problemləri. // Dielectric properties of composites based on magnetic micro- and nanoparticles and bentonite. (Gəncə Dövlət Universiteti 2018).
- Discovery Science Research International Research-to-Practice Conference. //Temperature dependence of magnetic parameters of composites modified with magnetic particles. (Petrozavodsk 2020).
- IV European Science forum International Research-to-Practice Conference. // The effect of particle size on the magnetic properties of composites based on bentonite and magnetic nano- and macroparticles. (Petrozavodsk 2020).
- During seminars of the Department of Physics of the Ganja State University, 2019.
- During seminars of Laboratory 1.8 "High voltages physics and technology" of the Institute of Physics of the Azerbaijan National Academy of Science, 2019.
- During the scientific seminar of the Institute of Physics of the Azerbaijan National Academy of Science, 2021.

Scientific publications. 13 scientific papers have been published on the subject of the dissertation, 9 of them being the scientific articles (4 of them are included in the Impact Factor and

SPRINGER international index system), and 4 of them – conference material.

Structure and scope of the dissertation: The dissertation paper consists of an introduction, four chapters of the main conclusions and a list of references. The paper is presented on 162 pages, including 9 tables, 16 figures, 77 graphs, and a list of references consisting of 136 titles.

The dissertation research was carried out at the Institute of Physics of the Azerbaijan National Academy of Science in the Laboratory 1.8 "High voltages physics and technology".

The content of the paper.

The introduction covers justification of the subject relevance of the dissertation paper, statement of the paper goal and the tasks to be solved, outline of the main provisions submitted for defense, statement of the practical value and scientific novelty of the results obtained, as well as summary of the dissertation content in chapters.

The first chapter is devoted to a review of the literature data on bentonite. The composition of bentonite clay $Al_2[Si_4O_{10}](OH)_2 \cdot nH_2O$ requires special attention, since it has a multicomponent composition and 32% of the total weight is Si, Fe-4.43%, Md-2.22%, Al-8.29%, etc. The silicon-oxygen tetrahedron $[SiO_4]^{4-}$ is the main structural unit of clays. These structures are bonded to the $Mg(OH)_2$ or $Al(OH)_3$ layers by weaker ionic forces, compensating for the negative charge of the complex anion.

The literature data analysis shows that the structures, as well as the physical and magnetic properties of nanocomposites based on polymers, magnetites and bentonites have not been adequately studied. A range of tasks with the relevant solution has been identified, and the purpose of research for this dissertation paper has been substantiated.

The second chapter covers the application of percolation theory to the study on the passage of alternating current in a percolated medium – a dielectric bentonite matrix with Fe_2O_3 ferromagnetic filler. Electric and magnetic interactions in a percolated medium are investigated based on the Efros–Shklovskii theory. The percolated medium (p-Fe_2O_3 and (1-p) - BT) was placed in a weak magnetic field, with ferrite particles isolated from each other by a dielectric layer. Analyzing the theoretical results, the values of the magnetic permeability of **μ, μ' and μ″** and **σ** of percolated medium, with different proportions of Fe_2O_3 filler, are calculated in this paper.

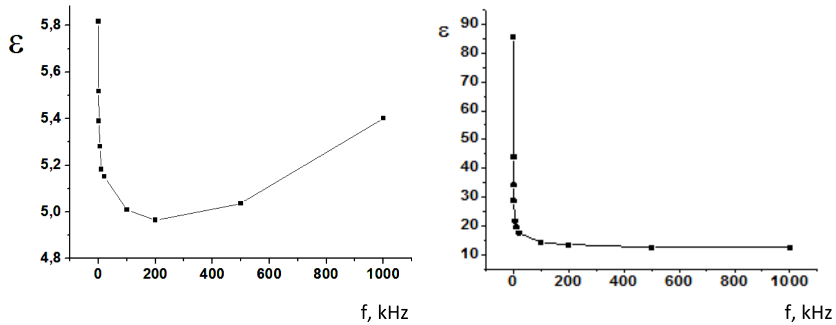
Magnetic susceptibility measurements of magnetic composites by the Faraday method, the methods of synthesis of bentonite- and polymer-based compositions, as well as composites based on bentonite and magnetic particles (Fe_2O_3 ferrites) are described. A more simple and versatile mixing method is used to mix the primary products of the polymer and Fe_2O_3 filler, resulting in a homogeneous mixture of components. The mixing process is carried out in dry form by means of micro-mills. Hot pressing, extrusion and deposition are mainly used to obtain composite nonlinear bentonite-based resistors. The hot pressing method expands the scope of application of nonlinear resistors. For example, you can create elements to limit overvoltage in high-voltage devices. The hot pressing method helps to synthesize samples with different thicknesses, etc.

The third chapter is devoted to the study of frequency and temperature dependences of the dielectric and electrophysical properties of bentonite samples on an oscillating electric field.

To study the frequency dependence of the dielectric parameters of bentonite composites, the composites were made of bentonite and polyethylene powders, previously ground in a Fritsch ball mill with porcelain balls. Composites were made of a homogeneous mixture of components by hot pressing at a temperature of 140°C and a pressure of 15 MPa. The content of composites varied in the range of (5-70)% BT and (95-30)% PE, respectively. The thickness of the samples was (150-180) μm.

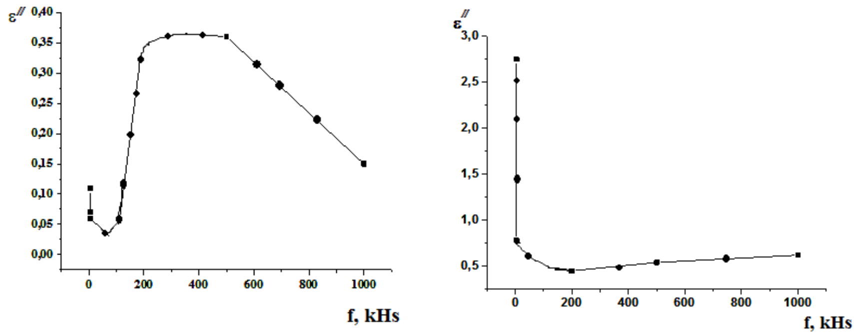
As a result of the study, a pronounced dispersion of dielectric parameters was established in the composites (Graphs 1, 2). The frequency dependences of ε' and ε'' indicate the occurrence of several types of polarization in the composite material when exposed to its oscillating field, caused by the heterogeneity of the material.

Dipolar interlayer polarizations of Maxwell-Wagner (Graph 2) are manifested in this dependence. The values ε and ε" of pure bentonite and bentonite composites are shown in Table 1.



a) **b)**

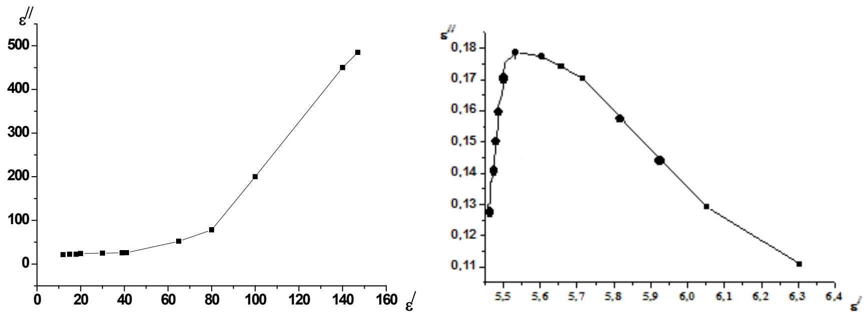
Graph 1. The dependence of dielectric permeability on the frequency of the oscillating field. a) 5% BT + 95% PE, b) 55% BT + 45% PE



a) **b)**

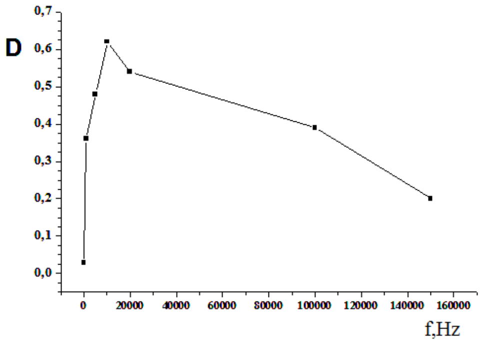
Graph 2. Frequency dependence of the imaginary part of dielectric permeability in the oscillating field
a) 20% BT + 80%PE b) 40% BT + 60% PE.

In the dependence of **ε, ε″** and **D** on the frequency **(**Graphs 1, 2, 3, 4), we can see that the maximum level is observed at low frequency values, indicating the appearance of interfacial polarization due to interlaying charges at the interface of polyethylene and bentonite. Graph 3 shows the dependencies $\varepsilon'' = f(\varepsilon')$ described by the Cole-Cole diagram. The difference between the diagram and circles at high frequency values becomes apparent. It is explained by availability of many relaxation times due to the heterogeneity of this composite material, as well as the formation of reach-through conductivity. In this dependence, the phenomena of dielectric relaxation, predicted by the Debye model, were not detected. For composites with more than 40% bentonite, this dependence $\varepsilon'' = f(\varepsilon')$ indicates the existence of interlayer polarization in this material.



a) b)

Graph 3. Cole-Cole diagram for composites a) 70% BT + 30% PE b) 20% BT + 80% PE

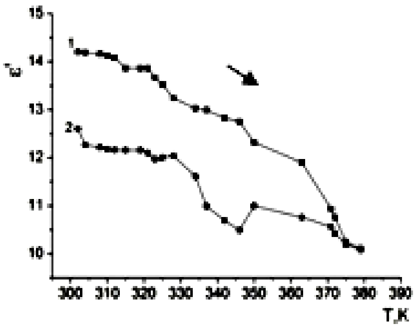


Graph 4. The frequency dependence of dielectric losses for the composite with 55% BT + 45% PE.

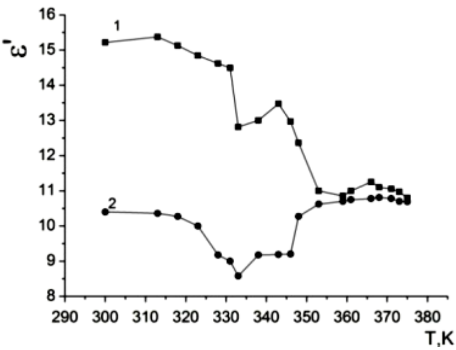
Table 1. The value of the dielectric permeability and the imaginary part of the dielectric permeability " of pure bentonite and bentonite composites**.**

f, kHz	Pure bentonite		5% BT + 95% PE		30% BT + 70% PE		55% BT + 45% PE		70% BT + 45% PE	
	ε	ε"	ε	ε"	ε	ε"	ε	ε"	ε	ε"
0,025	1117,6	858,53	5,9	0,14543	8,9	0,45	85,44	25,3	558	535,33
0,5	644,54	196,43	5,52	0,06622	8,53	0,31	43,94	19,7	255,6	232,69
1	597,76	155,82	5,39	0,05389	8,34	0,2749	34,2	14,1	136,8	106,83
5	514,6	100,92	5,58	0,0558	8,64	0,2674	28,81	10,7	105,6	76,47
20	483,40	81,02	5,21	0,05666	8,1	0,2335	21,65	6,1	58,8	34,98
100	470,41	74,322	5,6	0,42578	7,97	0,2309	19,47	4,9	47,4	25,56
200	400,24	70,91	5,02	0,49152	7,78	0,1787	17,58	4,12	39,36	18,97
500	384,64	75,44	4,98	0,31729	7,72	0,1697	14,16	2,78	25,83	10,41
1000	337,1	87,87	5,05	0,2183	7,82	0,1716	13,51	2,3	23,646	8,21

In the temperature dependence of the dielectric parameters and the electrical conductivity of the composites, a temperature hysteresis was detected (Graph 4, a,b,c,d). A phase transfer (T > 360 K) of the polymer matrix can be considered as an explanation. When cooling from high temperature to 360K, the dependence curves ε', D and σ and the heating curves coincide. It means that the temperature hysteresis occurs at a temperature of <360 K. Moreover, ε', D and σ (Graph 4, a,b,c,d) accepts different values at the same temperature values. These values are more in heated samples, than in cooled ones. The detected effect is related to the asymmetry effect of the temperature evolution of electrically active defects. We see the increase in the activation energy with temperature rise (the heating process) as the common pattern of the obtained dependencies. This increase causes the transitions of charge carriers to new energy levels. But when the temperature decreases (the cooling process) to room temperature (in our case) the activation energy decreases, due to which the Fermi levels inside the forbidden zone of the sample start to shift. Therefore the trapped charges are released, thereby changing the dielectric and electrophysical properties of the medium. This behavior of the composite can be associated with thermally stimulated process of charge redistribution at the particle-matrix interface, its accumulation in deeper traps and, as a result, the occurrence of nonequilibrium medium states. We know that highly-filled composite systems are very sensitive to temperature and frequency changes. They may be of interest for practical application in various technical fields, for example, in temperature sensors, etc.



a)



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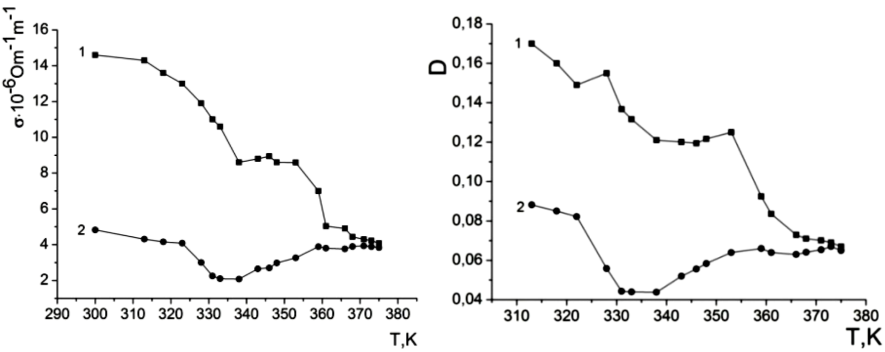
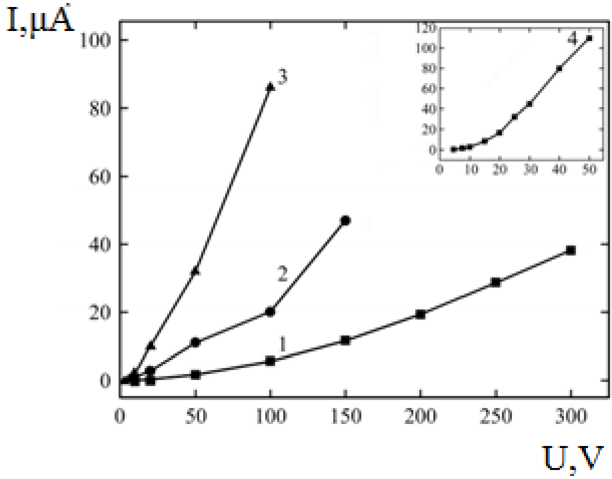


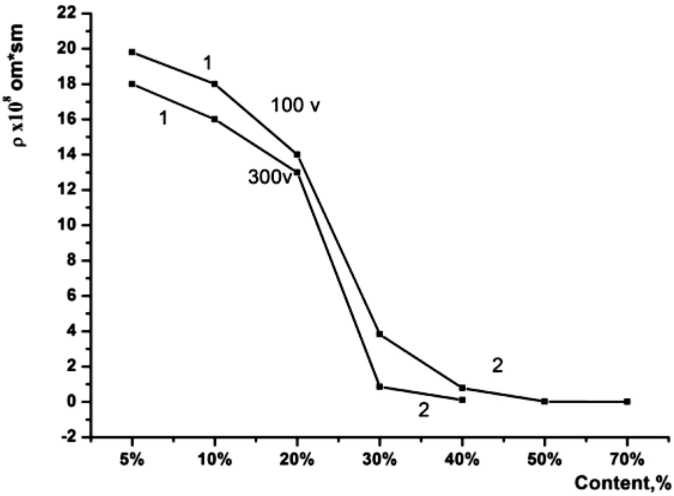
c) d)

Graph 5. The dependence of the real part of dielectric permeability on the temperature at f=1 MHz for composite **a)** 30% BT + 70%PE. **b)** 50%BT+50% PE. 1-heating, 2-cooling. **c)** electrical conductivity from temperature at f=1 MHz for a composite with 50% MMT + 50% PE. 1-heating, 2-cooling.

The nonlinearity of VAC is a distinguishing feature of semiconductor materials. It is associated with near-contact phenomena, as well as with the high-field effect. For this purpose, the VAC and ρ resistivity were studied in all samples. It turned out that VAC of the studied composites is nonlinear, and the VAC nonlinearity is pronounced at BT >30% (Graph 6), i.e. the VAC of bentonite resistors has varistor nature. It was found that for pure bentonite, the VAC has also nonlinear nature **(**Graph 6-(line4)). As we can see from the Graph 7, despite the different values of the applied voltage, the dependence of resistivity on the percentage of filler is exponential. Part of the curve (1) in Graph 7 corresponds to a large value ρdetermined by the resistance of the polymer. With an increase in the percentage of filler, the value of ρ decreases exponentially (Part 2). They can be used in the future to develop various low-voltage, low-energy and other elements for application in microelectronics.

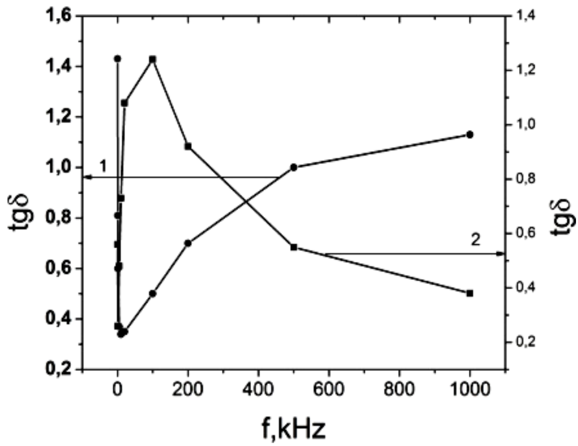


Graph 6. Volt-ampere characteristics of composites with different filler content: 1- 50% BT + 50% PE; 2- 60% BT + 40% PE; 3- 70% BT + 30% PE; 4-100% BT

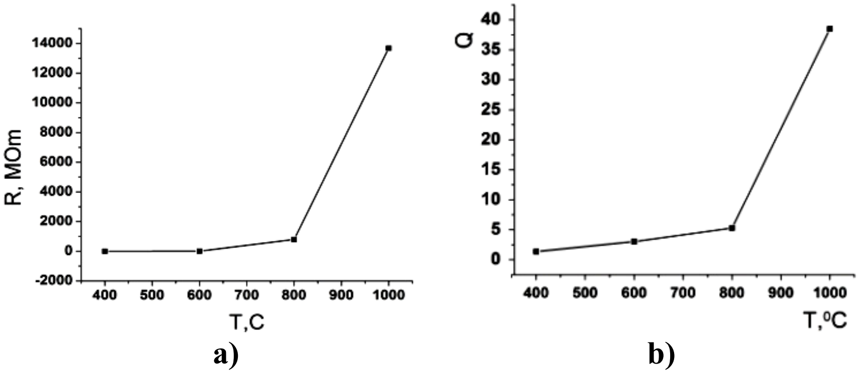


Graph 7. The dependence of electrical resistance of the composite on the percentage of filler (at 100 V and 300 V).

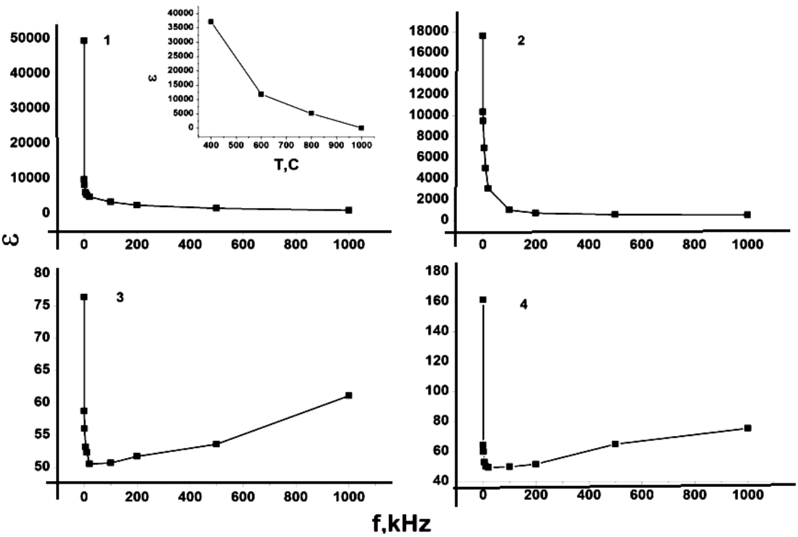
Disk-shaped samples with a thickness of 1.5 mm and a diameter of 7 mm were made on the basis of BT at room temperature; the electrophysical properties were studied. The resulting disks were pressed at 1 hPa, without heating, and five of them were annealed at 400°C, 500°C, 600°C, 800°C, and 1000°C in the RH15/15 furnace. After annealing, the electrophysical and dielectric properties of the samples were studied. It turned out that the annealing temperature strongly affects the electrophysical properties of bentonite (Graphs 8-10). The dielectric permeability and dielectric losses decrease as the annealing temperature increases. For the sample annealed at a temperature of 500°C, $tg\delta$ increases with increasing frequency, reaching a maximum at f=150kHz, then steadily decreases (Graph 8). The dependence of the dielectric permeability on the frequency has a dispersed nature $\varepsilon = f(F)$. The dielectric permeability reaches the highest value (ε=50,000) on a sample that has not been annealed, while the lowest value (ε=39) is reached on annealed one at 1000°C (Graph 10). Bentonite resistance increases, Q-factor increases (Graph 9). This in turn increases the likelihood of their practical application to produce high-voltage and high-frequency devices.



Graph 8. Dependence of dielectric losses on the frequency of the oscillating field: 1-T = 25°C, 2-T = 500°C



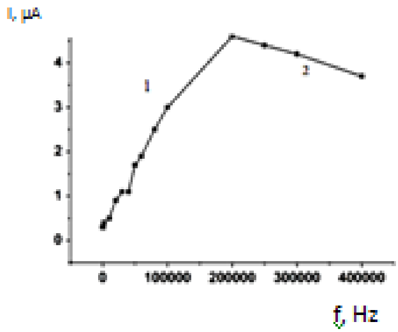
Graph 9. Dependence of a) electrical resistance b) Q-factor on the annealing temperature.



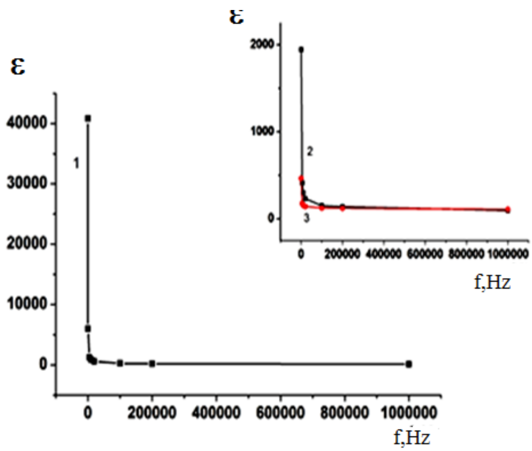
Graph 10. The dependence of the dielectric permeability on the frequency at different annealing temperatures.

The change in the active resistance was studied based on the bentonite samples modified at 3000 rp/m, 6000 rp/m, and non-modified ones, under the influence of an oscillating field frequency. The size of bentonite particles after modification at 3000 rp/m was

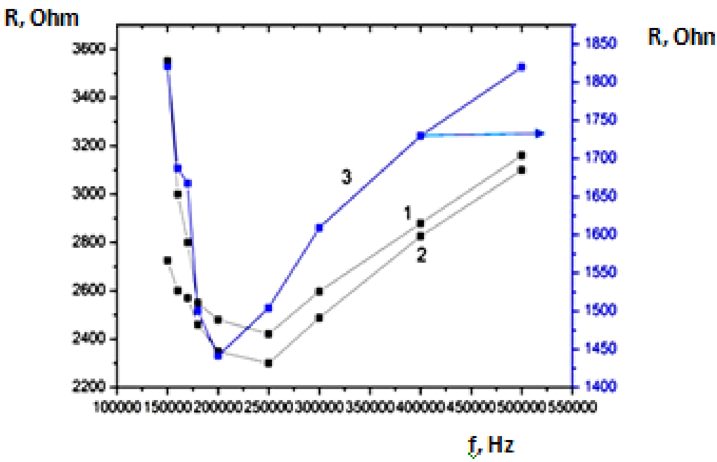
(440-560) nm, and at 6000 rp/m - (140-260) nm. Disks with a diameter of 7.2 mm and a length of 4.1 mm were made by pressing. Further, the VAC of all samples, the dispersion of dielectric parameters, as well as the dependence of resistance on frequency at a temperature of 300 K were studied. For the dependence of the electric current on the frequency, it turned out that with an increase in the oscillating field frequency, the value of the electric current increases, reaching maximum (Graph 11, area 1) at *f*=200 kHz, and with a further increase in *f* (Hz), the value of the electric alternating current decreases to a minimum (Graph 11, area 2). Graph 12 shows the frequency dependences of the dielectric permeability for non-modified and modified samples. As we see on the Graph, this dependence has a dispersed nature. And Table 2 provides the values of ε for all samples, showing clearly the effect of the modification degree on these values. A decrease of ε with an increase in the modification degree became apparent. We believe that the reason for the decrease of ε is the crushing of bentonite particles during the grinding process, contributing to an increase in the surface area, and, accordingly, an increase of the current in the samples ($I = envS$) and a decrease of the resistance in the sample ($R_{ak} = \frac{1}{\sigma}\frac{l}{S}$).



Graph 11. Frequency dependence of the oscillating field current for modified bentonite at 6000 rpm (U=1,14 V).



Graph 12. The dependence of the dielectric permeability on the field frequency for 1 – non-modified, 2 and 3 – modified bentonite.



Graph 13. Dependence of the resistance on the frequency of the oscillating field: 1 – non-modified bentonite, 2 – modified bentonite at 3000 rpm – №.1, 3 – modified bentonite at 6000 rp/m – №.2 (U=1.14V)

Table 2. Value of ε for non-modified and modified bentonite.

f, kHz	ε Non-modified bentonite (No.1)	ε Modified bentonite, 3000 rev/m (No.2)	ε Modified bentonite, 6000 rev/m (No.3)
0,025	40800	20400	5920
0,5	6000	1944	464
5	1224	412,8	176
10	856,8	300	155,2
20	592,8	231,6	142,56
100	255,6	150	124,16
200	180	138	121,6

Grinding of bentonite powder particles (during modification of powders) causes a strong friction between the particles, and as a result they get very hot. This heating evaporates the OH group and water molecule, leading to a decrease in the polarity and, consequently, a decrease in the dielectric permeability of the samples (see Table 1). As you can see in the Graph 13, with increasing *f*, R_a decreases to a minimum at *f*=200 kHz for bentonite modified at 6000 rp/m, and *f* = 250 kHz for samples of non-modified bentonite and bentonite modified at 3000 rp/m.

The active resistance grows in the high frequency area because of the skin effect. The experimental results obtained can be used as an electronic frequency converter in the area of a drastic fall in active resistance and as an excess-voltage suppressor during an increase in active resistance.

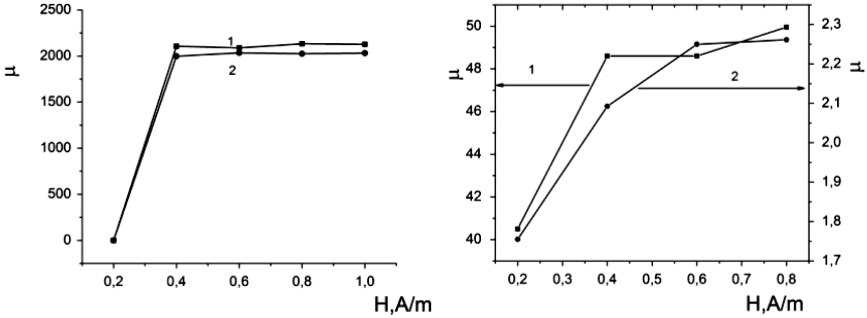
The fourth chapter. This chapter covers the study of the magnetic properties of composites based on magnetic particles (Fe_2O_3) and bentonite, as well as the application of percolation theory to study the electrophysical and magnetic properties of the percolated medium. The components used were previously modified in a FRITSCH type mill:

- A certain amount of bentonite was modified within 30 minutes at 6,000 rp/m.
- Modification of ferrite particles was carried out in the following modes

   a. 10 minutes at 3,000 rp/m (M1), $d_{3000} = 1.35\ \mu m$
   b. 10 minutes at 6,000 rp/m (M2), $d_{6000} = 0.68\ \mu m$

Further, mixing the components, disk-shaped samples were obtained by pressing, 16 mm long and 7 mm in diameter. The percentage of composite samples obtained was as follows:
60% M1 + 40% MB, 40% M1 + 60% MB, 50% M1 + 50% MB, 60% M2 + 40% MB, 40% M2 + 60% MB, 50% M2 + 50% MB

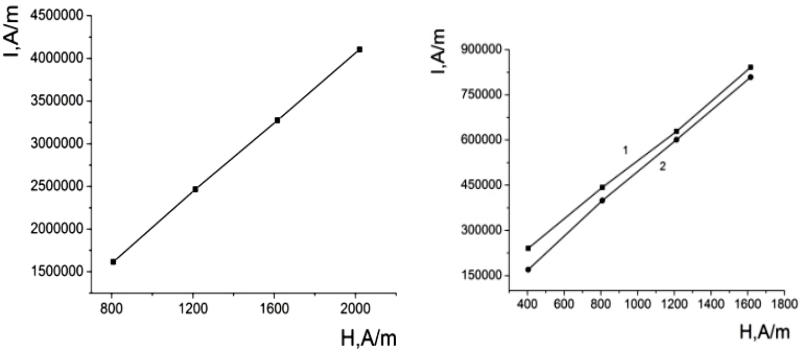
It was demonstrated that regardless of the percentage content and modification of components, an increase in the intensity of the oscillating field causes the increases in the magnetic permeability μ of the composites with 60% (Fe_2O_3) reaching its maximum value, and then tends to saturation with an increase in the field. In the dependence of $\boldsymbol{\mu}$ on the frequency in composites with 40% BT + 60% (Fe_2O_3), a decrease is observed in $\boldsymbol{\mu}$**.** The reasons for the change in the magnetic parameters of the composites studied were established. The effect of the modification degree of components on the magnetic properties of composites has been established. Specifically, in composites with a modification of magnetic particles at 3000 rpm and 6000 rpm, regardless of the percentage of components, the magnetic properties differ; in composites with a modification of magnetic particles at 3000 rpm, the values of the intensity of magnetism and magnetic permeability are 1.2 times more than at 6,000 rpm (Graphs 14-15). It turned out that with an increase in the intensity of the oscillating field, the value of intensity of magnetism increases regardless of the percentage of components, the value of magnetic permeability reaches its maximum, as well as saturation with further increased field.



a) b)

Graph 14. The dependence of the magnetic permeability on the magnetic field strength. a) f=500 Hz, 1-60% M1 + 40% MB, 2-60% M2 + 40% MB. b) 1- f = 2 kHz; 2- f = 20 kHz.

Samples with high values of magnetic permeability and low losses in the low-frequency region can be used as magnetic materials for radio components in high-frequency equipment because of high magnetic permeability and low losses.

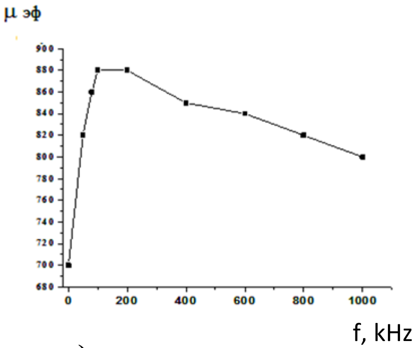


a) b)

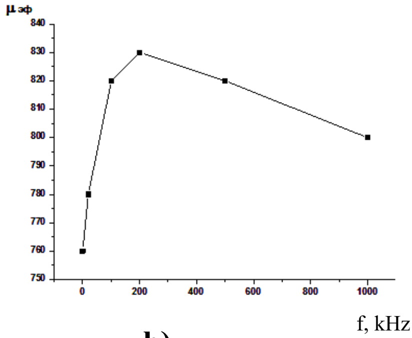
Graph 15. The dependence of the intensity of magnetism of composites on the magnetic field strength a) at f = 500 Hz b) at f=20 kHz 1 – at 3000 rp/m, 2 – at 6000 rp/m.

Samples with low values of magnetic permeability in the high frequency region are used in the creation of radar-absorbent materials.

Electrophysical and magnetic properties of percolated media were investigated using percolation theory. Composites modified by magnetic particles may be promising materials for practical applications, since under the action of fields of different nature in them a mechanical connection between clusters of ferrite particles and fillers is observed, i.e. such composites will possess magnetoelectric properties. Therefore, when studying the magnetoelectric properties of composites based on magnetic particles and bentonite, it is important to know the position of the percolation threshold which is one of the main characteristics of the percolation system serves as the percolation threshold pc. According to the effective field theory, the percolation threshold for spherical metal and dielectric particles in a three-dimensional system is 0.33. If granules have different sizes, the percolation threshold increases both in the two-dimensional and three-dimensional cases. It is believed that the formation of large clusters of different shapes, leading to an increase in the percolation threshold, is due to the attraction between the granules. The attraction between them is related by Coulomb and magnetic interactions. In magnetic systems, the process occurs differently. Single-domain particles form large chains while closing the magnetic flux. As a result, the percolation threshold rs increases due to the formation of large clusters in granular compounds. The dependences of ρ and σ on the percolation threshold are studied for composites, as well as the frequency dependences of the effective magnetic permeability of the studied percolated medium (Graphs 16-17). It was demonstrated that with the approach to the percolation threshold $p_c = 0.35$, the resistivity decreases, the conductivity increases. This suggests that an increasing number of individual ferromagnetic nanogranules in (p)Fe_2O_3 −(1-p) MBT composites connect forming separate clusters of Fe_2O_3 granules in the MBT matrix (Graph 17). Composite magnetic materials with a drastic decrease in magnetic permeability, are successfully used in the manufacture of radar-absorbent materials with an increase in the frequency of the magnetic field.



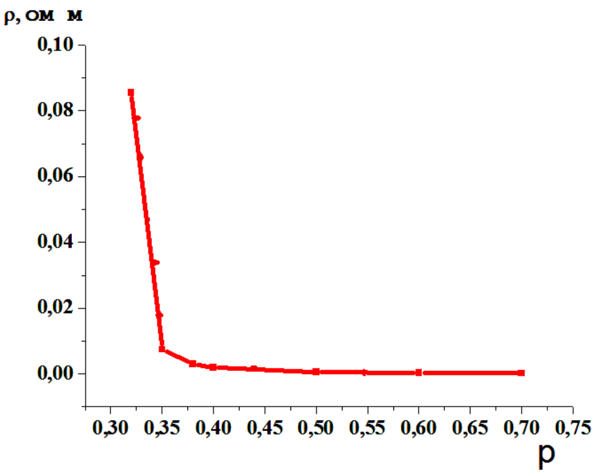
a)



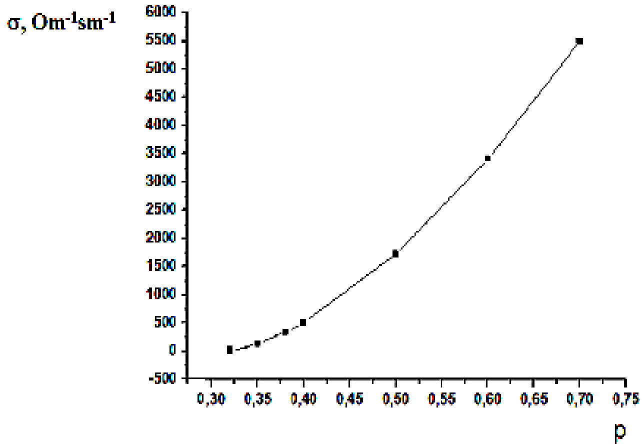
b)

Graph 16. Dependence of the effective magnetic permeability on the frequency for the composite:

a) 50% $(M_1)Fe_2O_3$ + 50% BT b) 60%(M2) Fe_2O_3+40% BT at H=660 A/m.



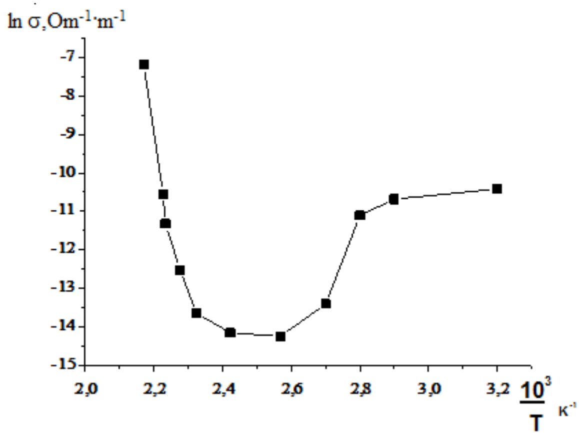
a)



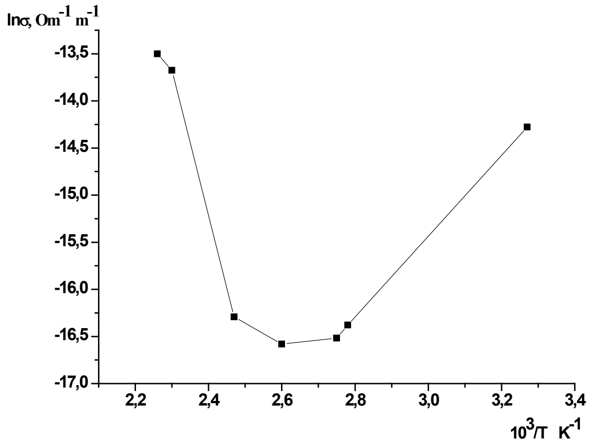
b)

Graph 17. Of the dependence of a) resistivity of ρ and b) electrical conductivity σ on the percolation threshold for composites (x)Fe_2O_3 − (1-x) BT at room temperature.

The temperature dependences of conductivity for samples (Graph 18) were studied: **№.1**-50% (M_1) Fe_2O_3 + 50% MBT, **№.2**-60% (M_2) Fe_2O_3+40% MBT. Note that the size of magnetic particles at 3000 rp/m (M_1) is greater than at 6000 rp/m (M_2) (d_{3000} = 1.35 μm, d_{6000}= 0.68 μm). It was demonstrated that for the studied samples, the dependences $\ln\sigma=f(\frac{10^3}{T})$ have a similar nature, i.e. the value of σ decreases and reaches a minimum, with increasing temperature, then with increasing temperature the value of σ increases. The dependencies $\ln\sigma=f(\frac{10^3}{T})$ indicate a semiconductor nature. For the studied samples, the activation energies were determined by the formula: ΔE = 0.23 tgα, eV. along the slope of the straight lines in the intrinsic conductivity section, and with increasing degree of modification, the activation energy increases, and lnσ decreases. The value of the activation energy for sample No. 1 E_a = 1.1 eV, and for sample No. 2 E_a = 2.4 eV, respectively. In addition, it was found that the degree of modification affects σcomposites, namely: for sample No. 1σ = 3· 10-5 Om^{-1} m^{-1}, for sample No. 2σ = 6· 10-7 Om^{-1} m^{-1}, accordingly.



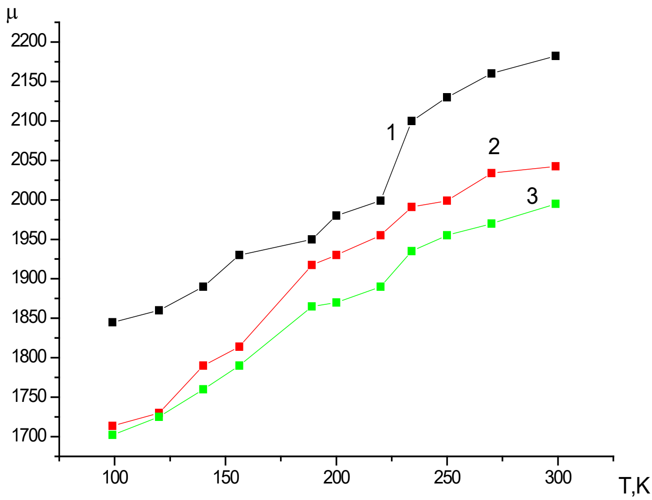
a)



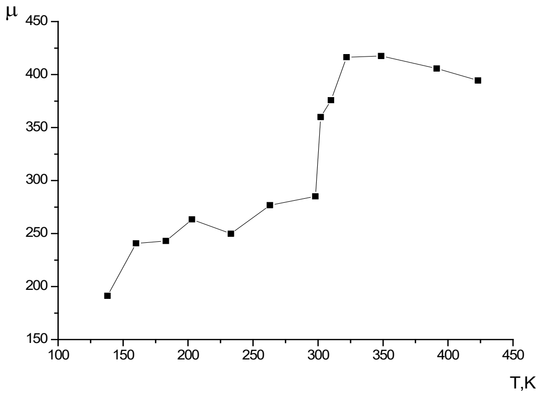
b)

Graph 18. The dependence of electrical conductivity on temperature for composites with 50% Fe_2O_3 + 50% BT and 60% Fe_2O_3 + 40% BT.

Temperature dependences of magnetic parameters of bentonite composites with Fe_2O_3 particles are studied. It turned out that the magnetic permeability increases $\mu$with increasing temperature and reaches a maximum value, and then decreases with increasing temperature. Thus, for composites №1, μ with increasing temperature, it grows and reaches its maximum value (Graph 19). For composites № 2, μ with an increase in temperature, it grows to a maximum at T = 340 K, and then decreases with an increase in temperature. (Graph 20).



Graph 19. Dependence of magnetic permeability on temperature for composite with 50% Fe_2O_3 + 50% BT at 3000 rpm, 1- H=602 A/m, 2- H=1200 A/m, 3-H=1800 A/m

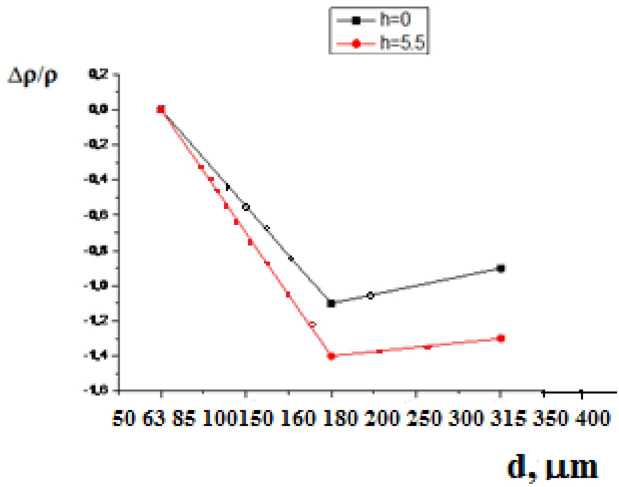


Graph 20. The dependence of the magnetic permeability on the temperature for the composite with 60% Fe_2O_3 + 40% BT at 6000 rpm. H=602 A/m, f= 200Hs.

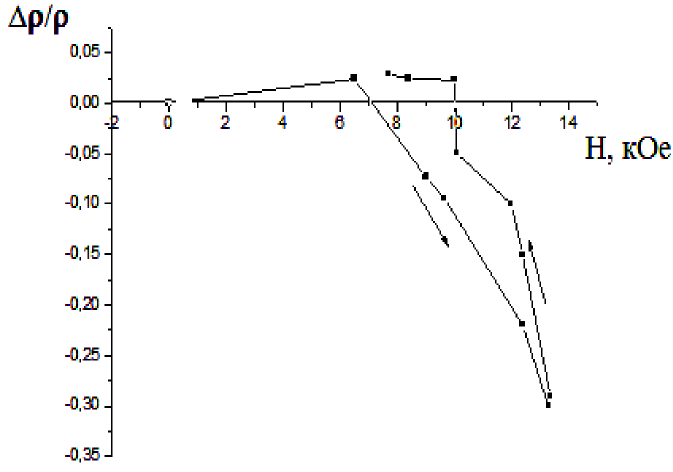
The effect of particle size on the magnetic characteristics of bentonite-based composites and Fe_2O_3 magnetic nanoparticles has been investigated. Using a FRITSCH planetary mill and a sieve, the following magnetic particles were obtained:

1. d < 63 μm,
2. 63 μm < d < 100 μm,
3. 100 μm < d < 160 μm,
4. 160 μm < d < 250 μm,
5. 250 μm < d < 315 μm,
6. 315 μm < d < 400 μm

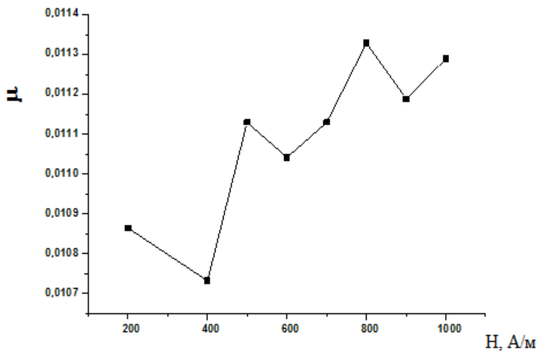
The studied composites with a height of 4 mm and a diameter of 7 mm were obtained from a homogeneous mixture of component powders by cold pressing at a temperature of 300 K. The dielectric parameters as well as the magnetic permeability were investigated on all samples. The dielectric parameters were measured with a digital imitance E7-20 in the frequency range $(25\text{-}10^6)$Hz, and the magnetoresistance value with a teraohmmeter type B7-06. The dependences of magnetoresistance on the magnetic field strength were studied in all samples. It was demonstrated that regardless of the value of the applied magnetic field and the particle size, negative magnetoresistance is observed. Besides, the value (NMR) decreases as particle size with increases, reaches a minimum value at d = 160-250 µm, and then grows again (Graph 21). The reason for the decrease in resistance with an increase in particle size lies in the fact that the number of conductive particles increases with an increase in particle size, thereby increasing the conductivity and as a result, the resistance value decreases. The further increase in magnetoresistance is most likely caused by the increase in the particle size due to their nodulization, as the number of current carriers decreases, and the conductivity decreases and the resistance increases, respectively. With an increase in the magnetic field, the MR becomes negative and with a further increase in the magnetic field MR increases towards a positive value (Graph 22).



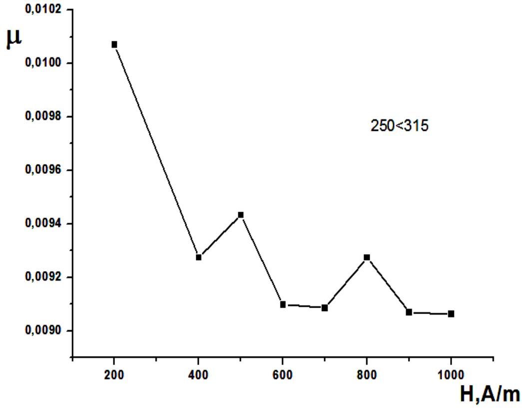
Graph 21. Dependence of magnetoresistance on particle size



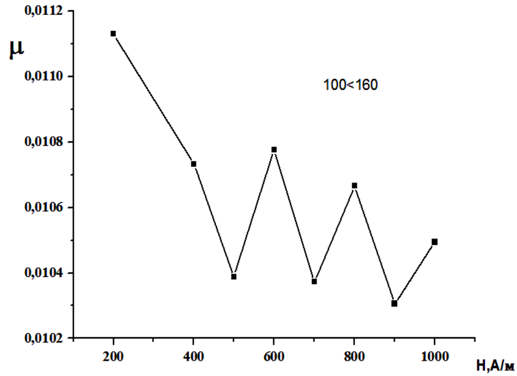
Graph 22. The dependence of the magnetoresistance on the value of the magnetic field for the composite with 50%Fe_2O_3+50% MBT.



Graph 23. The dependence of the magnetic permeability on the value of the magnetic field for the composite with 50% Fe_2O_3 + 50% BT(d<63μm).



a)



b)

Graph 24. The dependence of the magnetic permeability on the value of the magnetic field for the composite with 50% Fe_2O_3 + 50% BT. a) 250 µm < 315 µm b) 100 µm < 160 µm

The obtained result is explained under the assumption that both clusters and isolated granules of magnetic particles simultaneously exist in composites. At the same time, they are characterized by different values of magnetic anisotropy and the presence of a dipole-dipole – interaction between clusters and the closest granules.

RESULTS

1. A pronounced dispersion of dielectric parameters was found in bentonite composites with a polymer matrix. In the low frequency range of 25 Hz-100 kHz, values of ***ε*** decrease**.** For the samples up to 40% BT, the values of ε", with increasing frequency in the low-frequency region decrease, first slowly and then drastically. They reach a minimum value, and then with increasing frequency go up to maximum, with a further increase in the frequency they decrease, and with the increase of the filler content percentage, the observed maximum shifts to the high-frequency region.

2. The effect of the concentration of BT particles on the VAC and on the resistivity of bentonite composites with polymer filler has been established. The resistivity decreases exponentially with increasing concentration of BT particles. Nonlinearity of VAC is expressed in composites with a polymer matrix at BT >30%.

3. The presence of temperature hysteresis of the dependences of dielectric parameters and conductivity of composites with 50% BT + 50% PE, 40% BT + 60% PE is established. Systems of highly-filled composites are sensitive to temperature and frequency changes. During the heating process, the dielectric parameters decrease with increasing temperature.

4. For the composites with 50% Fe_2O_3+50% MBT and 60% Fe_2O_3+ 40% MBT:

- At a temperature of (300-500) the dependence $ln\sigma=f(10^3/T)$ indicates a semiconductor nature; the conduction mechanism in the studied composites has a zonal nature.
- For composites with 50% Fe_2O_3 + 50% MBT, the ***μ*** increases with rising temperature and reaches a maximum value, and the μ of the composite with 60% Fe_2O_3 + 40% MBT reaches a maximum at T=340K, and then decreases with rising temperature. The intensity of magnetism increases with increasing temperature, reaching a maximum value, and then decreases with increasing temperature. The magnetic moments of composites increase with increasing temperature, reach a maximum at T = 430 K, and then

decrease with increasing temperature. It was demonstrated that the main reasons for the decrease in magnetic permeability are: 1 – eddy currents created by self-induction EMF; 2 – magnetic losses; 3 – internal magnetic field created by free poles of randomly distributed magnetic particles.

5. With the approach to the percolation threshold $p_c = 0.35$, the resistivity decreases. An increasing number of individual ferromagnetic nanogranules in (p) Fe_2O_3−(1-p) MBT composites connect forming separate Fe_2O_3 clusters in the BT matrix, which combine and form a continuous grid of clusters.

6. Reducing the particle size changes the electrophysical, magnetic and dielectric parameters of composites. On a sample with modification of ferrite particles at 3000 rp/m:

50% *Fe_2O_3* + 50% MBT and 60% Fe_2O_3 + 40% BT values of dielectric permeability, magnetic permeability and electrical conductivity $\sigma=3 \cdot 10^{-5} Ohm^{-1} m^{-1}$ more than on the sample at 6000 rpm 50% *Fe_2O_3* + 50% BT, 60% Fe_2O_3 + 40% MBT, σ=6 ·10-7 $Ohm^{-1} m^{-1}$.

7. Regardless of the value of the applied magnetic field and the particle size, negative magnetic resistance is observed in the studied composites. It decreases with an increase in the particle size, reaching a minimum value, and then growing again.

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