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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**THE ROLE OF RELAXATION AND THERMAL IN THE
FORMATION OF PIEZO-, PYROELECTRIC EFFECTS IN
POLYMER-FERROPIEZOCERAMIC COMPOSITES**

Specialty: 2203.01 - Electronics

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GENERAL DESCRIPTION OF THE WORK

Relevance of the research topic. Currently, in the foreground is the creation of multifunctional materials, that is, smart materials that meet the growing requirements of all areas of technology, including military systems. The solution of this important problem is mainly carried out by the creation of smart materials based on semiconductors, ferroelectric ceramics, polymers and liquid crystals. An analysis of the experimental results shows that it is impossible to satisfy the growing demand for technology and military materials by synthesizing only new individual smart materials. That is why, combining the capabilities of a large number of different active and passive dielectrics, smart materials with higher characteristics are synthesized based on them. As an example, micro- and nanoscale ferro-piezo phase composites with a polymer matrix can be cited. The multiphase composition of the composites leads to the appearance of electronic, polarizing, deformation and chemical effects (phenomena) at the interface. A characteristic feature of multiphase systems is the presence of relaxation oscillators in them with different relaxation periods, the properties of which can be easily controlled by the action of an electric field, temperature, and mechanical stresses. Each relaxation oscillator has its own specific relaxation time and determines the macroscopic characteristics, stability and operating temperature range of a smart composite material. Therefore, when developing the technology of polymer-ferro-piezoelectric composites, it is necessary to take into account their relaxation and thermal properties. In our opinion, the piezo ceramic phase with a certain dipole moment behaves as a relaxation oscillator both before and after polarization and is actively involved in the formation of piezoelectric, pyroelectric, and electrode effects in the composites studied by us. The experimental results showed that the polymer phase is not passive and that the development of technologies to increase the activity of the polymer phase in composites (electrets, piezoelectric and pyroelectrics) is an important task in active composite materials science. In addition,

the change in the characteristics of polymeric materials, including composites, under the effect of new, external physical and chemical factors, should be taken into account when developing sensors (converters) and electrical devices. Recently, the widespread use of organic polymers in piezoelectric and pyroelectric materials, optoelectronics, thermal devices and alternative energy sources, the simplicity of the production technology and economic efficiency put them at the foreground as a promising material. Together with this, targeted modification of existing polymers is considered as a promising scientific trend. Therefore, more accurate and extensive studies are needed to determine the relationship between the physical and chemical structure of polymers and their properties. One of the important directions of these studies is the almost unexplored role of thermophysical, especially relaxation, phenomena in the formation of piezoelectric and pyroelectric effects in polymer-multicomponent piezoelectric composites. Experimental and theoretical results show that the mentioned relaxation phenomena allow developing and optimizing the technology for producing polymers, composites based on them (for example, multifunctional active piezoelectric and pyroelectric materials based on polymers).

Object and subject of research:

The main object of research of the dissertation are polymers as organic phase with high electro-physical and thermal properties (HDPE, PVDF, F-23, F-26) and multicomponent ferroelectric ceramic of various structures as non-organic phase.

The main subject of the research is the study of piezo- and pyroelectric effects in composites consisting of these polymers and ferroelectric ceramic.

Aims and purpose of the research:

The main objective of the dissertation is to establish the role of relaxation and thermal phenomena in the formation of piezoelectric and pyroelectric effects in composites based on polar (F-23, F-26, PVDF) and non-polar (HDPE, PP) polymer matrices and multicomponent piezo phases ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$).

The following issues have been solved to achieve the goal:

- The establishment of a connection between the polarization of the components of the composite with a polarized polymer-multicomponent piezoelectric phase, polarized by the combined action of the electric field strength (E_p) and temperature (T_p), and its macroscopic parameters:

- Determination of the effect of electron-ionic, polarization processes occurring in the polymer phase of a composite with a fluorine-containing (F-23, F-26) polymer matrix and a multicomponent piezo phase ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$) on the phenomena occurring in the piezo phase;

- Establishing the effect of the potential difference of the electret ($U_{e.p.f}$) and the electret charge (Q_e) on the macroscopic parameters of the composite;

- The formation of effective and inefficient quasineutral systems during polarization in a composite with polar (F-23, F-26, PVDF) and non-polar (HDPE, PP) polymer matrix and a multicomponent piezo phase ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$) and their influence on the macroscopic characteristics (d_{ij} , g_{ij} , K_{ij} , ϵ_{ij} , $\tan\delta$) of composites;

- The relationship between the domain structure of the piezophase of the composite we studied and its piezoelectric and pyroelectric properties (d_{ij} , g_{ij} , K_{ij} , γ_p , γ_p/ϵ);

- The role of space charges in the polarization process in polymer-based composites (F-23, F-26) and anomalous polarization;

- Experimental determination of optimal polarization when combined with a strong electric field (E_p) and temperature (T_p);

- ensuring the stability of the electret charge state of the studied composites by physical and chemical methods;

- Determination of the role of relaxation oscillators in the corresponding phases in composites with a polymer matrix (F-23, F-26, PVDF, HDPE) and a multicomponent piezo phase polarized under the combined action of a strong electric field, temperature, and electric discharge plasma.

Research methods:

The main reason why polyolephins (HDPE, PP) and fluorine-containing polymers (F-23, F-26, PVDF) were used as the organic phase is the fact that they have high electro-physical, electronic and thermal properties compared to other polymers. The choice of multicomponent ferro-piezoceramics as the inorganic phase is due to the possibility of a relatively simple modification of their structures.

Specially designed devices were used for polarization of studied composites and their subsequent determination of piezo- and pyro coefficient. The dielectric properties of the sample were measured with E7-8 and E8-4 devices. Then a TSD device was used to study the thermostimulated depolarization current spectra of samples. For the modification of the components of the composites the presence of strong polar groups (C=O, C-O-C, OH) in the polymers (HDPE) characterized by the VIIY-10 determined by infrared spectroscopy (IR). Calorimetry DSC 204 F1 manufactured by NETZSCH was used to determine the thermodynamic parameters of the analyzed samples. As well as, the thermal conductivity of the composites was measured on the NETZSCH STA 449 F1 Jupiter device in the absence of mass loss or even mass loss of the researched samples. The thermal conductivity of the samples was then measured using the LINSEIS THB-100 Hot Bridge method/

The main provisions for the defense:

1. The relationship between the degree of polarization of the piezo phase of composites with a fluorine-containing polymer matrix (F-23, F-26) and the multicomponent piezo phase ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$) and their macroscopic parameters.

2. Determination a relationship between the domain structure of the piezo phase of a composite with a polar and non-polar (F-23, F-26, PVDF) polymer matrix and a multicomponent piezo phase and appearing in them piezoelectric and pyroelectric properties.

3. Determination of possible mechanisms of electrical, thermal and mechanical properties after polarization in composites with a polymer matrix (F-23, F-26, PVDF, HDPE, PP) and a ferro-piezo phase with different structures (R, T, R + T).

4. Determination of the possible mechanisms for the formation of piezoelectric, pyroelectric effects in composites with a polymer matrix (F-23, F-26, PVDF, HDPE) from the spectra of thermally stimulated depolarization (TSD) currents.

5. An experimental study of the domain, dipole orientation arising in the course of polarization in the composites studied by us;

6. The role of space charges arising during polarization in polymer-based composites (F-23+PbZrO₃) and possible mechanisms of anomalous polarization.

7. Determination of the relationship between relaxation and thermal properties in composites consisting of a highly polar polymer phase (F-23, F-26) and multicomponent piezo ceramics (PbTiO₃-PbZrO₃-PbNb_{2/3}Zn_{1/3}O₃-PbNb_{2/3}Mg_{1/3}O₃).

8. Formation of new phases (relaxation oscillators) between the polymer and piezo ceramics during polarization and the determination of the mechanisms of their influence ultimately on the macroscopic and microscopic characteristics of the composite we studied.

The scientific novelty of the research:

1. A relationship has been established between the degree of polarization and the electret charge state and the macroscopic parameters of composites consisting of a polymer matrix with high dielectric constant and polarity (F-23, F-26) and multicomponent ferro-piezoceramics (PbTiO₃-PbZrO₃-PbNb_{2/3}Zn_{1/3}O₃-PbNb_{2/3}Mg_{1/3}O₃).

2. The formation of effective and ineffective quasineutral systems in composites with a polymer matrix (F-23, F-26) and a multicomponent piezo phase (PbTiO₃-PbZrO₃-PbNb_{2/3}Zn_{1/3}O₃-PbNb_{2/3}Mg_{1/3}O₃) in the polarization process and their effect on the macroscopic characteristics of the composite have been presented.

3. A relationship between the piezoelectric, pyroelectric, electro-physical and physic-mechanical parameters in the studied

composites polarized under the combined effects of electric field strength (E_p), temperature (T_p) and modified under the influence of electric gas-discharge plasma have been determined.

4. The effect of anomalous polarization in composites with a polymer matrix with high dielectric constant (F-23, F-26) and one-component piezo phase ($PbZrO_3$) have been revealed.

5. The heat capacity (c_p), thermal expansion coefficient (α), thermal conductivity (λ) in composites consisting of a polar polymer matrix (F-23, F-26) and multicomponent piezo ceramics have been studied, and the relationship between the piezoelectric coefficient (d_{ij}), electric field intensity (E_p), pyroelectric coefficient (γ_p) have been established for the composite we studied.

The theoretical and practical significance of the research:

1. Experimental determination of electric gas-discharge plasma as a more efficient and new method of modification of composite materials.

2. Experimental determination of optimal polarization under the combined action of a strong electric field and temperature as a more efficient and new technological method.

3. Prediction of microscopic (sizes of lamellas, fibrils and spherulites) and macroscopic parameters (d_{ij} , g_{ij} , k_{ij} , γ_p) in the composites studied by us (F-26+ $PbTiO_3$ - $PbZrO_3$ - $PbNb_{2/3}Zn_{1/3}O_3$ - $PbNb_{2/3}Mg_{1/3}O_3$) using thermal, thermos-physical and plasma phenomena formed using various modification methods.

4. Priority of composites with a highly polar polymer matrix (F-23, F-26) and multicomponent ferro-piezoceramics ($PbTiO_3$ - $PbZrO_3$ - $PbNb_{2/3}Zn_{1/3}O_3$ - $PbNb_{2/3}Mg_{1/3}O_3$) in the direction of the development of new pyroelectrics, piezo electrics and electrets.

Approbation and implementation:

The results of the study obtained during execution of the dissertation work were presented at the following national and international conferences:

- 11th International Symposium on Ferroic Domains And Micro– to Nanoscopic Structures”, - Russia, Ekaterinburg, -2012, -pp. 183.
- 1st International Scientific Conference of young scientists and specialists, -Baku, Azerbaijan, -15-16 October, -2014, -pp. 235-237.
- The 5th International Conference on Control and Optimization with Industrial Applications, - Baku, - Azerbaijan, -27-29 August, -2015, -pp. 432
- International Science Forum. Nuclear Science and Technology, Almaty, September 12-15, - 2017, - p. 250 (in Russian).
- The 6th International conference on Control and Optimization with Industrial Application. -11-13 July,- Baku, - 2018, -pp. 240-242.
- Materials of the republican scientific conference on topical issues of energy training in energy specialties, Sumgayit, Azerbaijan, May 30-31, - 2019, p. 88-90 (in Russian).

Publications. According to the main results of the dissertation, 18 works, including 12 articles, 6 theses and conference materials were published abroad (“Science Citation Index”) and in republican scientific journal, conference materials. The list of works is given at the end of the abstract.

The name of the organization where the dissertation was performed. The dissertation was performed at the laboratory “Physics of Nano- and active composites” of the Institute of Physics of the Azerbaijan National Academy of Sciences.

Volume, structure and main content of the dissertation

The dissertation consists of an introduction, four chapters, results and a list of used sources of 132 items. The volume of work consists of 251079 characters, excluding figures, tables, graphs, applications and a list of references, contains 14 tables, 93 figures.

CONTENT OF WORK

In the **introduction**, the relevance of the topic of the dissertation is substantiated, the purpose of the research is formulated, the scientific novelty is indicated, the main provisions for the defense and practical significance of the work are stated.

The first chapter analyzes the piezoelectric, pyroelectric, relaxation, and thermal effects in composites consisting of polymers of various structures and ferro-pyroelectrics and the literature data on the relationship between them.

It has been shown that polymers (HDPE, PVDF, F-23, F-26) are subject to certain changes in their structure as a result of the influence of external factors (E_p , T_p and plasma method). Relaxation of the domain structure in different electro-physical conditions in piezoelectrics, which is another phase of composite is an important issue in the development of new piezoelectric composites. Recently, thermoactivation transitions in polymers and their effect on the macro and micro characteristics of the composite based on them have been widely studied. The development of nanotechnology and the study of their mechanisms allow us to correctly determine the resistance of a micro phase composite to external influences. Although the effect of adhesion and formation of chemical bonds between polymer and simple substances (Al, Ni, Co, Mn et.al) is well studied, multicomponent piezo ceramic with organic materials (polar and non-polar polymers, resins) are practically little studied. Polymer – $Pb(ZrTi)O_3$ - $\Sigma Pb_{1-\alpha}B_{\alpha}O_3$. As can be seen, the non organic component of multi-component were studied are oxygen-containing interactions between. The polymer and the electronegative B"-O cations control the relaxation and thermal effects in composite.

It was further noted that their electrothermopolarization is an important technological process for the composite to be a piezoelectric element and provides composite injection of electric carriers. Injected electric carriers control the relaxation processes in the polymer phase. These are related to the thermal effects present in polymer-segnetopyezoceramic composites. Injected

electric carriers control the relaxation processes in the polymer phase. These are related to the thermal effects present in polymer-segnetopyezoceramic composites. These parameters are directly related to the intensity of the thermal oscillation of macromolecules in polymer-segnetopyezoceramic composites. These parameters affect the price of piezo- and pyro-ratios of composites. The study also notes that the technology of great importance in terms of modification of polymers is their crystallization under the combined action of electric gas discharge plasma and temperature. In this method, the polymer creates oxygen centers of different origins in the chain of macromolecules of the matrix. Oxidation of macromolecules of the polymer matrix has a strong effect on its polarity, the state of electric charge, and the concentration of local levels in the quasic band of the polymer increases. Thus, any change in the structure results in the emergence of new local levels.

The samples studied then show the relationship between relaxation and thermal effects and electrical effects. These effects, both in the process of polarization and the application of piezoelectric and pyroelectric elements in various fields of technology, highlight the study of thermoelectric properties of these elements. It is known that the piezoelectricity (d_{33}) of piezocomposites is mainly determined by the residual polarization (Pr) of the domains after polarization, and is simply expressed as: $d_{33} \approx Pr \epsilon$ and $g_{33} = d_{33} / \epsilon$. These parameters should be changed so as not to reduce each other.

And the end of the chapter, as a result of the study of the existing literature, the issues to be resolved in the dissertation identified.

The second chapter is devoted to the getting of composites and their research methods. For this purpose, multi-component piezo ceramics of different structural (rhombohedral, tetragonal, heterogeneous) belonging to the family of zirconium-titanium-lead (ZTL) were taken as a polymer phase (HDPE, PVDF, F-23, F-26) and as a segnetopyezoceramic phase. Crumbs of polymer and segnetopyezoceramics which were the main

components of composites dimensions equal to 10-250 microns were used. As the initial stage of the composite getting process the crumbs of identical (homogeneous) press of these two components were obtained. For this purpose, to obtain crumbs of press the components were cut into small pieces and mixed in a dry mill. Then, a hydraulic press was used to obtain the composite by the hot pressing method. As a final step in the preparation of composite materials, the sample is polarized under the influence of electric field and temperature. The polarization of the composites was carried out with a special polarization device. In this case, the intensity of the electric field (E_p) given to the sample is limited by the electrical strength of the composite. The polarization temperature (T_p) was taken to be less than the melting temperature (8-10) K of the polymer phase. The piezo coefficient of the investigated composites was measured in a static mode by a special device. For this purpose, a circular sample is placed between the press poisons. In parallel to the sample, the Co capacitor was connected. It was put pressure in a certain amount to the piezocomposite by press and kept stable. When the applied pressure is taken from the sample, the load accumulated on the electrodes of the piezo-composite element loads the Co-capacitor and is numerically equal to the piezo coefficient. Also the pyro coefficient (γ_p) quasi of the pyroelectric materials we used was measured by static and dynamic methods. Using the method of dielectric spectroscopy to determine the dielectric properties ($\text{tg}\delta$, ϵ) of the studied composites in E7-8 and E8-4 devices at frequencies of 1 kHz and in the temperature range (293-473) K was appointed.

In the work it was also used the method of obtaining thermally stimulated depolarization (TSD) current spectra to determine the electric charge state of the composites, the concentration of unbalanced electrons injected into the composition during the polarization process, the activation energy of ionized local levels. In the composites we studied, the scheme of the device used for the study of TSD was given. During the experiment, the sample was heated at a rate of 5 $^{\circ}\text{C}$ /min (or 3

K/sec). Based on this method, it is possible to obtain information about the relaxation of electric charge carriers, dipole-orientation polarization and depolarization, stabilization of unbalanced electrons, mechanisms of orientation and deorientation of relaxants by linearly changing the temperature of the sample.

In addition, the following modern devices have been used to determine the role of thermal relaxation events in composites.

Differential scanning calorimetry (DSC) method was used to study the changes that occur during the heating of polymers and composites based on them, glazing, crystallization and melting. For this purpose, the samples used with the help of NETZSCH DSC 204 F1 (made in Germany) were studied. The temperature range of the device is (-180-700⁰C). The analyzed samples are placed in aluminum sockets. As a standard example, the heating rate of taken sapphire as 10K / min, the velocity of inert gas flow was taken as 20 ml / min.

The thermal conductivity of the studied composites was measured with the NETZSCH LFA 467 device. The temperature range of the device used is -100÷ 500 ⁰C. The samples were tested with the LFA 467 from 25 to 300 ⁰C with 50 K steps. The measurements were carried out in a special sample holder for thin samples (12,7 mm). Each sample was measured five times at each temperature step.

The thermal conductivity of the samples we used was measured by the Hot Bridge method on a LINSEIS THB-100 device. In addition, the thermal properties of the studied samples were analyzed thermogravimetric (TG) with the NETZSCH STA 449 F1 Jupiter device. The sample is heated to a certain temperature, then cooled and after cooling, measured with analytical accuracy. Thermogravimetric analysis up to 19 samples weighing up to 5 g at a time and can operate at temperatures up to 1000 ⁰C. The activation energy of the samples was calculated according to the TG spectrum.

The third chapter, shows the importance of studying the thermal and relaxation properties of composites, due to the expansion of the use of active composite materials, including

polymer-based piezoelectric and pyroelectric materials. So, these properties allow us to elucidate the role of processes occurring under the combined action of a strong electric field and temperature in composites consisting of piezoceramics, dispersed in a polymer. Note that the determination of the relationship between relaxation, thermal and electro-thermal properties is considered one of the main issues of composite materials science. The definition of such an interaction can explain not only the more accurate mechanism for the formation of piezoelectric and pyroelectric effects in the composites studied by us, but also contribute to their practical use, including the creation of composite based acoustic and electroacoustic transducers for various purposes. The most important factor in our work is the appearance of new phases (relaxation oscillators) in the process of polarization between the polymer and piezoceramics and the determination of the mechanisms of their effect on the macro- and microscopic characteristics of composite. Single-phase electron, electron-domain, and electron-dipole systems behave as important relaxation oscillators and determine the reorientation polarization (P_r). That is why the relaxation oscillators that exist both in the polymer matrix and in piezoelectric particles must be activated using polarization factors (E_p , T_p , t_p). Now let's look at relaxation effects that can affect the macroscopic parameters of composites with polymer matrices and multicomponent piezo phases. For this purpose in Figure 1 the distribution of macroscopic parameters of composites with polymer matrices and multicomponent piezo phases is presented. It can be seen from the figure that the dielectric permittivity (ϵ_{33}/ϵ_0) and the reorientation polarization (P_r) of the composite first increase with increase of $PbZrO_3$ volume, reaches a maximum value and then decreases. Similarly, the electromechanical coupling coefficient (K_p), the piezoelectric coefficient (d_{ij}) and the piezoelectric sensitivity (g_{ij}) of the composite increase linearly at first and then decrease. Possible explanation of such dependences in composites can be given by how the parameters of both phases change: numerous experimental results show that in order to increase the macroscopic

characteristics (d_{33} , g_{33} , K_p , $\text{tg}\delta$) of the inorganic phase of the composite – ferro- pezo ceramics, of particular importance the effect of electronegativity of the phases. In addition, based on experimental results, it can be said that in piezoceramics belonging to the ZTL (zirconium-titanium-lead) family, its electronegativity increases with growth in number of components.

It is seen from Fig. 2a, that in order to increase the electric charge state of ferro-piezoceramics, it is necessary to increase the number of their components and the electronegativity of cations. The polymer matrix, which is another phase of the composite, to increase the electric charge state was modified by a gas discharge plasma. Figure 2b shows the dependence of the piezoelectric module and the boundary charges for the HDPE+PbTiO₃-PbZrO₃-PbNb_{2/3}Mn_{1/3}O₃-PbNb₂MnO₃ composite on the electronegativity of the piezo phase cations.

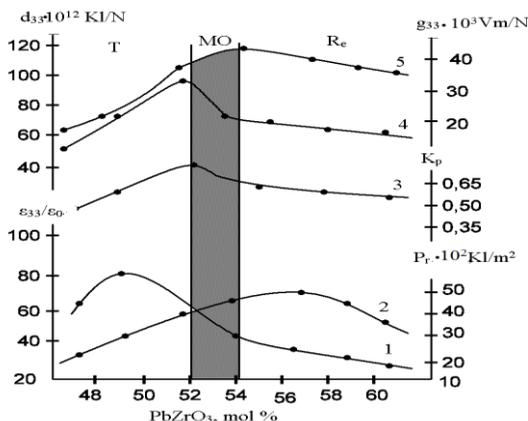


Figure 1. The dependence of the parameters of the F-26+PbTiO₃-PbZrO₃-PbNb_{2/3}Mn_{1/3}O₃-PbNb_{2/3}Zn_{1/3}O₃ composite on the concentration of its PbZrO₃ component: P_r(1), ε₃₃/ε₀(2), K₃₃ (3), d₃₃ (4), g₃₃ (5).

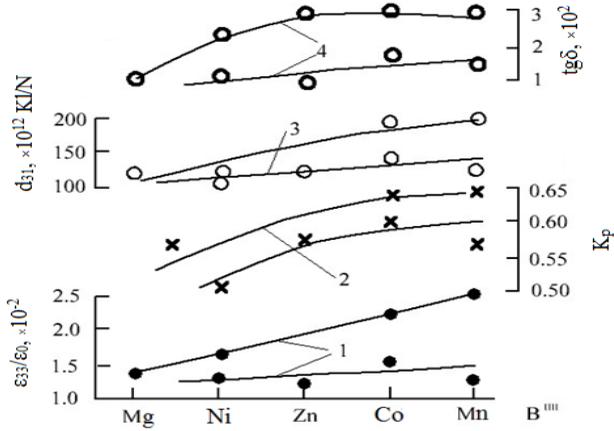


Figure 2a. Dependence of the main parameters of three ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3$) and four-component ceramics ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$) on the electronegativity of their cations.

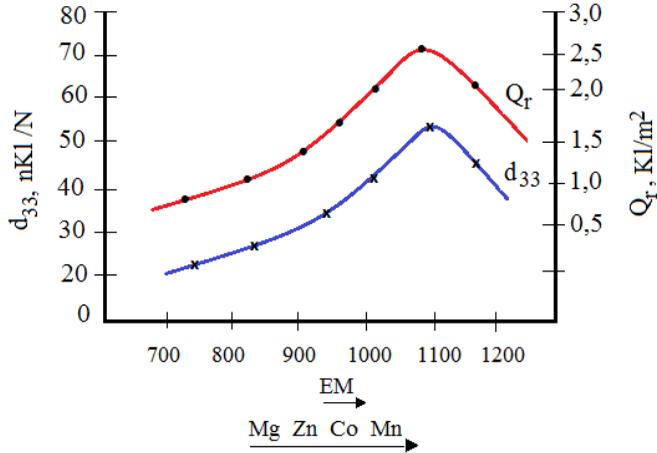


Figure 2b. Dependence of d_{33} and Q_r characteristics for the HDPE+ $\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3$ composite on the electronegativity of piezo phase cation.

These parameters increase with an increase in the electronegativity of cations, and reaching a maximum, decrease. Based on the results shown in Fig. 2a and 2b, it can be said that the main parameter of the composite – piezo coefficient (d_{33}) increases with an increase in the number of components of the piezo phase, at $n = 4$ it reaches a maximum, and with a further increase in the number of components, the piezo coefficient decreases (Fig. 3).

To determine the role of relaxation and thermal phenomena in the formation of piezoelectric and pyroelectric effects in the composites we studied, we used several techniques. In solving this problem, one should use factors of an electromechanical, thermo-physical nature (relaxation oscillators).

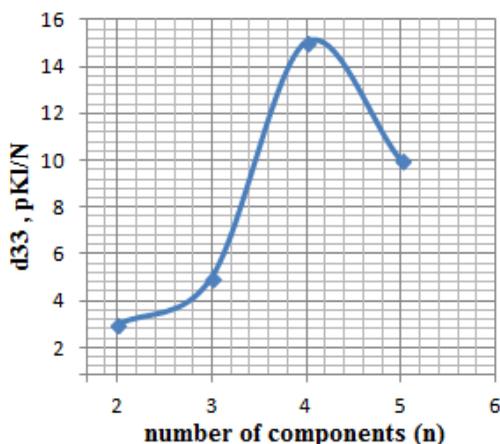


Figure 3. The dependence of the piezoelectric module (d_{33}) on the number of components (n) in multicomponent piezoelectric composites, $d_{33}=f(n)$: $n=2$ -F-23+PbTiO₃ - PbZrO₃; $n=3$ -F-23+PbTiO₃-PbZrO₃-PbNb_{2/3}Mn_{1/3}O₃; $n=4$ -F-23+PbTiO₃ PbZrO₃-PbNb_{2/3}Zn_{1/3}O₃-PbNb_{2/3}Mg_{1/3}O₃; $n=5$ -F-23+PbTiO₃-PbZrO₃-PbNb_{2/3}Zn_{1/3}O₃-PbNb_{2/3}Mn_{1/3}O₃-PbW_{1/2}Mg_{1/2}O₃.

It turns out that when the voltage is applied, the domain of the piezoelectric domain, which has a large volume and cost of

loading, is neutralized in the field conditions. As the electronegativity increases, d_{33} increases as design guidelines and then decreases.

The main reason for the formation of piezoelectric and pyroelectric effects in polymer-multicomponent piezoelectric composites is the formation of a quasineutral system formed by electrons injected during the polarization process (homo charges-relaxants) and effective domains (hetero charges-relaxants) that change direction in the direction of electric field.

Analysis of research on the basis of polymer-multicomponent piezo-phase composites shows that the presence of two relaxants is essential for the formation of electrets, pyro – and piezoelectric effects in composites. Otherwise, it is impossible to form these effects in composites.

The dipole moment generated by the quasineutral system under the influence of mechanical excitation determines the value of the piezoelectric modulus (d_{33}) of the composite. Therefore, there is an important relationship between the transfer of electrons, volume charges (ions) injected into the composite in the process of polarization and the orientation of the piezoceramic phase domains in the direction of the applied electric field. These events result in the formation of effective and ineffective quasineutral systems in composites (Figure 4) ¹. Figure 4 shows the electrical model of the piezoelectric element. This model combines the following stages:

- quasineutral system formed by injected free electrons with positive charges in the volume of the composite\
- a quasineutral system formed by electrons injected into the volume by domains.

When mechanical stress is applied, the first and second quasineutral systems have a certain dipole moment. Until you do this, the whole system is quasi-neutral. This means that under the

¹ Dadashov Z.A. Boundary effects in polymer composites-powered ceramics // Azerbaijan Journal of Physics, -2019, v. XXV, No. 3, - p. 20-21.

influence of mechanical stress, the system we are studying has a certain dipole moment, which determines the piezo coefficient. Quasineutral systems formed during the polarization process induce electric charges on the electrodes under the influence of mechanical stress. In this case, the electrons move in an external circuit and accumulate in capacitor. Creates positive charges on one plate of the capacitor and negative charges on the other plate. The load accumulate in the capacitor under the influence of mechanical excitation corresponds to the piezo coefficient of the composite we studied.

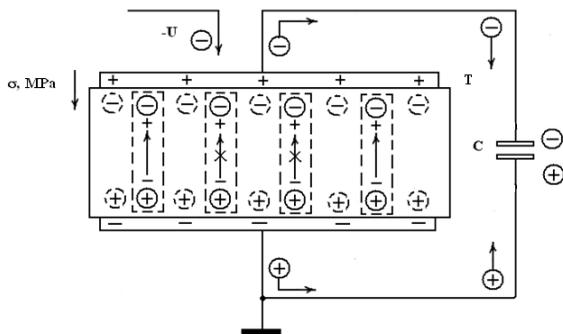


Figure 4. A simple model of a polarized polymer-multicomponent composite.

When identifying relaxation oscillators, it is necessary to use several directions:

- effective and ineffective relaxation oscillators formed in composites when combined with a strong electric field and temperature;
- quasineutral systems formed by electric charge carriers injected into the composite under the influence of a strong electric field, with dipoles and domains;
- relaxation oscillators formed in the composite under the effect of the electric gas discharge plasma, alongside with the formed low-molecular polar groups and macro radicals.

If we consider that most of the relaxation oscillators operate on a thermal principle, then it is more important to study the pyroelectric effect than the piezoelectric effect. Because in the piezoelectric effect, electromechanical phenomena are studied, and in pyroelectrics thermal effects are studied.

By examining $J = f(T)$ spectra of various structures and thermal stability, we can use the obtained results as a method of technological prediction. Fig. 5 shows the change in the pyroelectric current as a function of temperature in the form of a symmetric function $J = f(T)^2$.

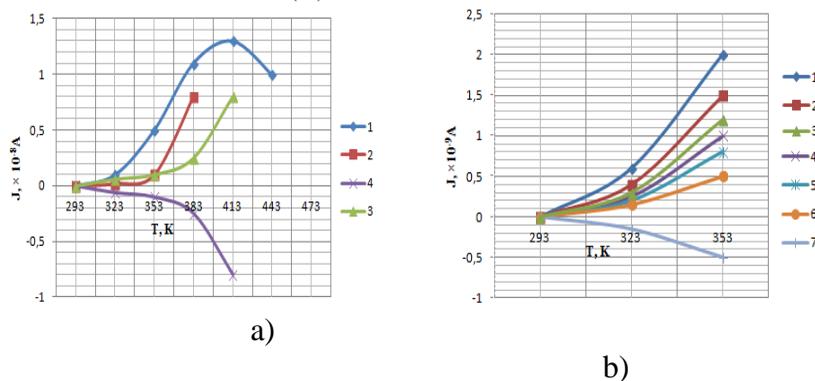


Figure 5. Temperature dependence of the pyrocurrent $J = f(T)$ for the composite $F-23+PbTiO_3-PbZrO_3-PbNb_{2/3}Zn_{1/3}O_3-PbNb_{2/3}Mg_{1/3}O_3$ (a); dependence $J = f(T)$ for numerous heating-cooling cycles for composite $F-23+PbTiO_3-PbZrO_3-PbNb_{2/3}Zn_{1/3}O_3-PbNb_{2/3}Mg_{1/3}O_3$ (b).

These spectra differ in terms of value and structure. In the first curve, the $J=f(T)$ pyrocurrent is of great value, while its stability is low and have extreme nature. However, in the subsequent heating-

² Курбанов М.А. Новая технология создания высокочувствительных сегнетопьезоэлектрических материалов на основе гибрида микро- и наноструктурированных полимеров / М.А.Курбанов, Ф.Н.Татардар, З.А.Дадашов [и др] // Журнал Технической Физики, - 2019, т. 89, вып 5, - с.744-748

cooling process, the pyroelectric current becomes exponential, quickly stabilizes, and has a symmetrical shape in shape, and the amplitude is much smaller than that of the first. Figure 5b shows the stable spectrum $J = f(T)$ after numerous heating-cooling cycles³. It can be seen from the graph that the symmetric curves 6 and 7 are stabilized after many cycles, and this spectrum was used in our work as a research method and allows us to optimize the pyrometric characteristics of the multicomponent piezo phase. So, symmetry is more important in this spectrum to get a stable pyroelement.

The fourth chapter, the role of thermal relaxation effects, which are important for formation of pyro- and piezoelectric effects and for the use of composites is studied in the following sequence: One of the factors affecting the macroscopic parameters of the composites studied by us (d_{ij} , γ_p , g_{ij} , etc.) is their coefficient of thermal expansion (α). As is known, this coefficient depends on the heat treatment of the composite, pressing pressure, as well as on the physical, chemical, and electron-ion processes occurring at the interface between the polymer phase and ferro-piezoceramics. Fig. 6 shows the effect of gas-discharge plasma on the temperature dependence of the thermal expansion coefficient. It can be seen from the figure that the thermal expansion coefficients of the composites studied by us, crystallized under electric gas gas-discharge, are very small. Modification of composites under the influence of gas-discharge plasma significantly reduces their coefficient of thermal expansion.

In addition, modification of the composite under the effect of gas-discharge plasma leads to reactions involving oxygen, creates macrophages with a certain dipole moment, and ultimately enhances the surface effects between pyroelectric particles

³ Дадашов З.А. Пироэлектрический эффект в гетерогенной системе полимер-сегнетопъезоэлектрик/ З.А.Дадашов, М.А. Курбанов, Г.Х.Гусейнова [и др] // Azərbaycan Milli Elmlər Akademiyasının xəbərləri, fizika –texnika və riyaziyyat elmləri seriyası,- 2016, c. XXXVI, №2, -s. 66 –72.

(adhesion). As a result, significantly reduces the thermal expansion coefficient of the composite.

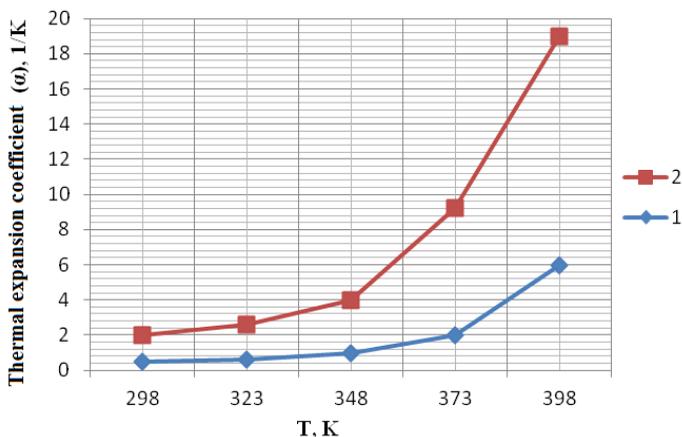


Figure 6. Temperature dependence of the coefficient of thermal expansion (α) of composites: 1- HDPE+PbTiO₃-PbZrO₃-PbNb_{2/3}Zn_{1/3}O₃-PbNb_{2/3}Mg_{1/3}O₃; 2 - F-23+PbTiO₃-PbZrO₃-PbNb_{2/3}Zn_{1/3}O₃-PbNb_{2/3}Mg_{1/3}O₃. The volume of the polymer phase is $\Phi = 80\%$.

In work, the effects of thermal treatment on polymer and composites based on them were studied with the use of a NETZSCH DSC 204 F1 differential scanning calorimetry. In this method we determine the temperature dependence of the heat absorbed or released by the material. Thus, the DSC method allows one to obtain information on temperature, enthalpy, entropy, the nature of relaxation transitions, specific heat and its change, and kinetic characteristics when the temperature changes⁴. Fig. 7 shows the initial DSC curves for HDPE and PVDF. On both

⁴ Dadaşov Z.A. Polimer-çoxkomponentli kompozitlərdə pyezo-, piroelektrik effektlərin formalaşmasında istilik effektləri// Enerjetikanın problemləri jurnalı, - Bakı: -2019, № 4, -s.71-76.

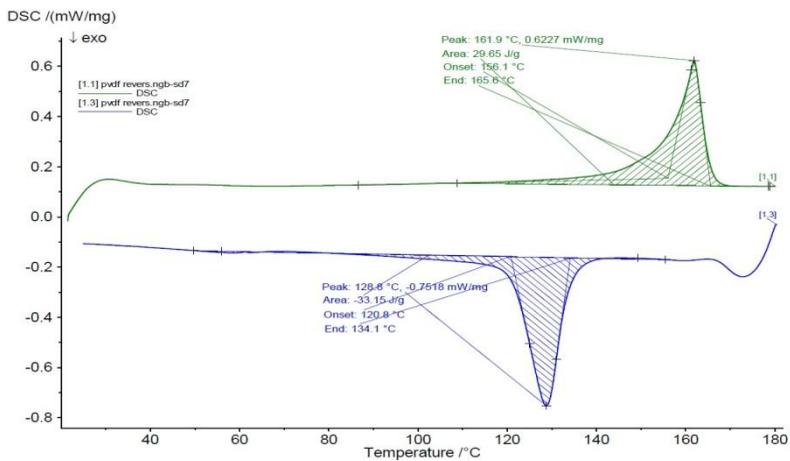
polymers, two peaks are observed during a single heating-cooling cycle. The main reason for this is that the polymers are subjected to oxygen destruction processes under the effect of thermal treatment and this process is observed at higher temperatures in the PVDF than in the HDPE. Using DSC, one can determine the glass temperature, which is an important parameter for the practical use of polymers. The results obtained are given in Table 1.

Table 1. Results of thermodynamic parameters of pure polymer obtained in DSC

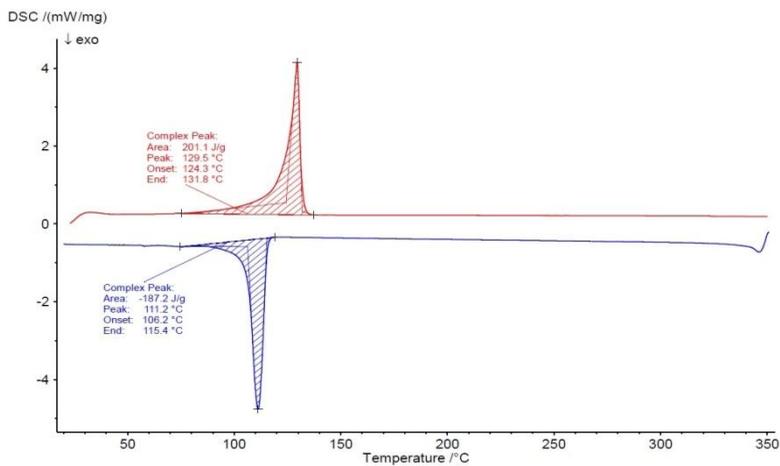
Polymers	Glass temp. (T_g) $^{\circ}\text{C}$	Meltingt emp. (T_m) $^{\circ}\text{C}$	Specific Heat Capaciy (c_p) $\text{J/g}\cdot^{\circ}\text{C}$	Thermal Conductivity (λ) $\text{W /m}\cdot^{\circ}\text{C}$	Enthalpy (ΔH) J/g	Thermal Charge (ΔS) J/K	Degrees of crys. (K), %
HDPE	100	124-131	1,8-2,7	0,33-0,53	201	2,36	4,75
PVDF	40	156-165	096-1,4	0,19	105	0,65	3,33

In work, we also investigated structural changes caused by thermal effects in composites consisting of polar (PVDF), non-polar (HDPE) polymers and various ceramics. For this purpose, DSC spectra of HDPE+PKR1 and PVDF+PKR1 composites are given in Figure 7. As can be seen from the figure, two maximum are absorbed here. The value of the first maximum is 128°C (approximately close to the melting temperature of the polymer), the value of the second maximum is 480°C (this is called the complex peak).

Using the results obtained in the DSC spectrum, the thermodynamic parameters of the composites were calculated using the following button

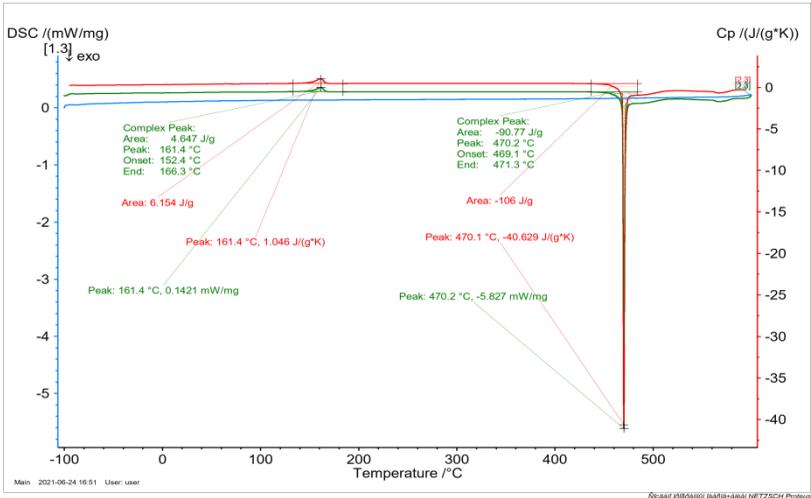


a)



b)

Figure 7. DSC spectra of pure PVDF (a) and HDPE polymers (b) .



a)

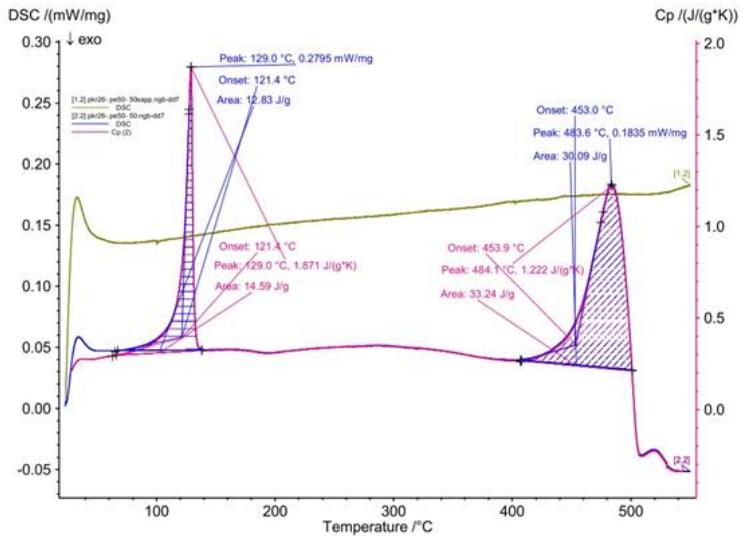


Figure 8. DSC spectrum for PVDF+PKR1 (a) and HDPE+PKR1 (b) composites.

$$\text{Changing of enthalpy: } \Delta H = S_{Area} = \int_0^T c_p dT \quad (1)$$

Changing of entropy:
$$\Delta S = \frac{\Delta H}{T_t} = \int_0^T \frac{c_p}{T} dT \quad (2)$$

Degree of crystallinity (K,%):

$$K = \frac{|Peak Area(melt)+Peak Area (cooling.ry)|}{Enthalpy (melt 100\% cryst)} \cdot 100\% \quad (3)$$

The maximum observed in the DSC curves are related to the processes in the polymer phase and the interfacial boundary under the influence of high electric field, temperature and electric gas discharge plasma:

- change of structure;
- interphase interaction;
- as the interphase interaction increases, the degree of crystallinity decreases, as well as macromolecules lose some of their freedom;
- as the process of electro-thermo-polarization take place under the influence of piezoelectric particles, the amorphism of the composite is generally reduced.

Therefore, in thermos-activation processes, for example, in spectra of TSDC, DSC, DTA new peaks are observed and also the peaks slide in the direction of high temperature.

Based on the results obtained, we can say that the maximums observed in the DSC curve are related to the change of structure in the polymer phase and the phase the interaction between the phases. The samples we studied in the work how thermal diffusivity changes depending on the temperature. For this purpose, the thermal diffusivity of three samples (PVDF + PKR1, PVDF + PKR8, PVDF + PKR57) was measured at the Thermophysical Properties section of the NETSZCH Applied Laboratory in Germany. The obtained results show that thermal diffusivity (D) decreases with increasing of the temperature. Thermal diffusivity of all samples is in the range from room temperature to approximately 150°C (maximum deviation is 4.4%). After 150 °C, samples 2 and 3 show greater thermal

diffusivity compared to sample 1. Figure 9 shows the temperature dependence of thermal diffusivity during the second heating of the composites that we use. Sample 1 has the lowest thermal diffusivity of 0.226 mm²/s, sample 2 (5.8% higher at room temperature) and sample 3 (19.5% higher at room temperature) are shown sequentially. In our opinion, the different result obtained during the first and second heating processes is due to the hardening effects.

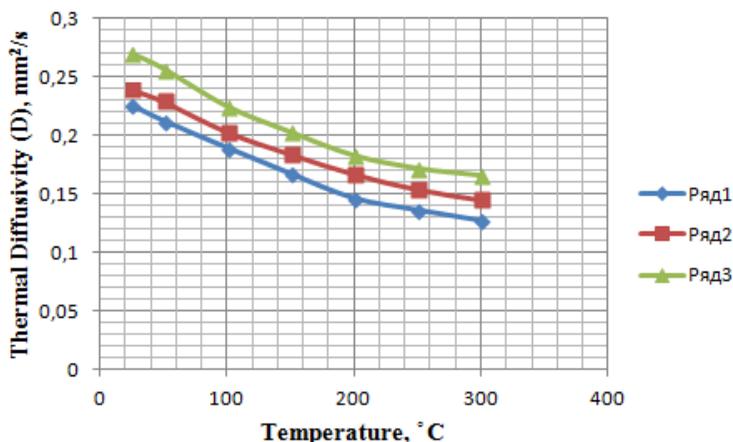


Figure 9. Thermal diffusivity of composites during heating from 25 °C to 300 °C (1st heating). 1-PVDF+PKR1; 2 - PVDF+KR57; 3 - PVDF+PKR8.

Knowing the specific heat capacity, density and thermal diffusivity of the samples we studied, as well as their thermal conductivity was calculated using the following formula:

$$\lambda(T) = \rho(T) \cdot c_p(T) \cdot D(T) \quad (4)$$

The results obtained are given in Table 2.

Table 2. Thermal conductivity of the studied samples

Samples	Structure	Density (ρ) q/m^3	Specific heat capacity (c_p) $J/q \cdot ^\circ C$	Thermal diffusivity (D) mm^2/san	Thermal conductivity(λ) $W/m \cdot K$
PVDF+PKR1	R	2,44	0,534	0,226	0,294
PVDF+PKR8	T	2,44	0,449	0,239	0,262
PVDF+PKR57	R+T	2,44	0,740	0,270	0,488

In addition the thermal conductivity (λ) of the composites we studied was measured by the Hot Bridge method and the results obtained were presented in the study. Temperature conductivity (D) and specific heat capacity (c_p) were also determined by this method (Table 2).

The samples we examined using the differential thermal analysis (DTA) method indicate weight loss as well as changes without mass loss. As an example, one can specify changes in the crystal structure, melting, glassing, and so on. For this purpose, the DTA spectra of samples of pure polypropylene (PP) and PP + PKR12 are presented (Fig. 10 a and b). The results show that composites with the smallest mass loss have a rhombohedral structure.

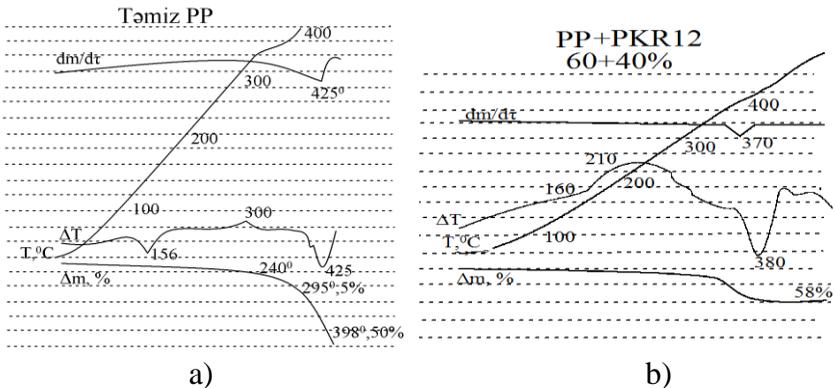


Figure10. DTA spectra for pure PP (a) and PP + PKR12 (b) samples.

In composites with a tetragonal structure, this indicator is relatively large (in comparison with composites with the PKR3M phase)⁵. We believe that the mass loss (Δm) will decrease with increasing intermolecular interaction or electronegativity of the phases. In addition, the determination of the temperature of the glassy state corresponding to composites with the PKR-3M phase has a practical value in addition to their physical properties and allows to determine the polarization temperature which determines the properties of the composites. This effect, in addition to its physical essence has practical value. So, it allows you to determine the polarization temperature, which determines the properties of the composites. In addition, the dielectric strength for the composites with high mass loss reduces. Obtaining information on the parameters of E_p and T_p of composites leads to the optimization of their polarization modes.

In the composites we investigated, the thermogravimetric analysis (TGA) method was used to determine the role of thermal relaxation phenomena in the formation of piezo- and pyroelectric effects. The TG spectra for the PVDF + PKR1 composite in Fig. 11 show the exothermic effects at different temperatures (200 °C, 450 °C, 470 °C). The high temperature peaks observed on the graph determine the mass loss.

⁵ Дадашов З.А. Релаксационные, термические и межфазные эффекты в композитах полимер- сегнетопъезокерамика различной структуры / З.А. Дадашов, М.А.Курбанов, И.С.Рамазанова [и др] // Физика и Техника Полупроводников, - 2019, т.53, вып8, -с.1115-1121.

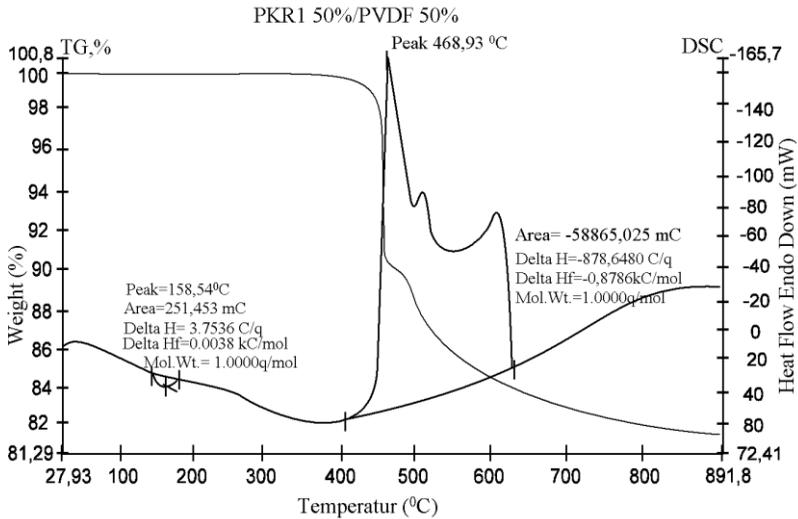


Figure 11. TG spectrum of PVDF + PKR1 composite.

The main results obtained in the dissertation work.

1. For the first time in composites with a polymer matrix of high polarity (F-23, F-26) and a multicomponent inorganic phase ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$), methods for effectively varying relaxation and thermal phenomena have been developed.
2. The main reason why these composites have high piezoelectric properties is the formation of relaxation oscillators of electronic character during polarization at the interface.
3. In composites with a polymer matrix of high polarity (F-23, F-26) and a multicomponent piezo phase ($\text{PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$) in the process of polarization at the interface the presence of direct proportionality between the concentration of injected charge carriers and pyro coefficients is established.

4. To obtain a stable pyroelement based on the composites we have studied, it is more important that the pyrocurrent has symmetry in the temperature-dependent spectrum and that this method is useful in selecting piezoelectric materials.
5. The thermodynamic parameters researched composites were studied by differential scan calorimetry and on the basis of them the possibility of creating new piezo-, pyromaterials with higher thermal properties was determined.
6. In polymer-multicomponent piezo phase composites, numerous pyrocurrent have been analyzed and a more accurate optimal polarization mode ($E_p=8\text{kV/mm}$, $T_p=413\text{K}$ and $t_p=0,5$ hours) has been set for the $\text{F-23+PbTiO}_3\text{-PbZrO}_3\text{-PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3\text{-PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$ composite.
7. In the analysis of the thermal properties of the sample we studied by the thermogravimetric method, it was determined that the composites with the lowest mass loss have a rhombedral structure and the materials based on them are distinguished by practical application at high temperatures.
8. The thermal conductivity of researched samples was studied by the hot bridge method and the increase in the thermal conductivity of the composites was determined by increasing the interaction between the polymer piezoceramic.

The main results of the dissertation are published in the following works:

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