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Matrix Active Micro- and Nanocomposites Based on the Polymer, Semiconductive and Ferropiezoceramic Materials

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1. Introduction

Active composite materials are a wide class of material used in radio engineering, electronics, optoelectronics, pyro- and piezotechnic. The possibility of application of created electrets, piezo- and pyroelectrics, posistors, piezoresistors, varistors, photoresistors, photovoltaic elements and photoelectrets based on the active composites is multiform beginning from various acoustoelectric transducers, acoustic generators, sensors of heat flow, image transducers, photoelements of information recording and storing, until using for radiation protection of spaceships, revealing of underwater objects, seismic and geophysics exploration, also for solving many problems of creating of alternative energy sources (for example, photovoltaic) and medical-biological problems.

At present, there are mainly four directions in area of creating abovementioned elements based on the solid dielectrics and semiconductors. First of them is connected with creating new ferropiezoelectric and semiconductive materials mainly based on the barium titanate, plumbum-zirconium-titanate (PZT), $A^{II}B^{VI}$, $A^{III}B^V$, $A^{III}B^{VI}$, $A^{IV}B^{VI}$, also semiconductors doped by rare-earth elements. Second direction is based on the synthesis of new polymer dielectrics revealing electret, piezo-, pyroelectric and photoelectric properties. Third direction is connected with creating various composite materials based on the polymer (matrix) dispersed by inorganic ferropiezoelectric or semiconductive fillers. Forth direction discovers new possibilities connected with creation various nanocomposite active materials including hybrid materials consisting of matrix nano- and micropiezoelectric composites.

The establishment of interconnection between characteristics of composite materials and properties of polymer, inorganic, ferroelectric and semiconductive phases is a key task on the way of solving of the very important problem of creating micro- and nanoelectric material. Numerous investigations of ferro- and piezoelectric materials have shown that the usage multicomponent piezomaterials based on PZT as inorganic phase is most perspective for obtaining high effective pyro-, piezoelectrics and electrics.

It should be noted that at present by variation of composition and number of components in PZT family it is impossible further to improve properties of piezo-, pyroelectric and electret materials. It is caused by that, the increase of piezo- and pyroelectric coefficients due to regulation (increase) of ferrossoftness and electromechanical characteristics is directly accompanied by a decreasing of pyro- and piezoelectric responses owing to increase of

dielectric constant. But the increase of ferrostiffness with aim of decrease of a dielectric constant is accompanied by a decreasing of piezo- and pyrosensitivity due to decrease piezo- and pyroelectric constants. So, an appreciable gain of characteristics of the piezo-, pyroelectric and electric ceramic materials isn't provided by application abovementioned technological methods.

The wide and various application of piezo- and pyroelectric dielectrics in electroacoustics, pyro- and piezotechnics in many cases demands to create large-size flexible transducers of various configuration. These demands aren't practically satisfied by application of inorganic ferroelectric materials and semiconductors. As it was noted, developments of composite materials with organic and inorganic components discover new possibilities in material science. At present, the numerous kinds of polymer materials with various physical-mechanical, electrophysical, thermophysical and photoelectrical characteristics are used as organic matrix [Furukawa T. et al., 1979; Hiroyoshi Ueda et al., 1986; Jamada T. et al., 1982;; Furukawa T. et al., 1976; Chinchurreta F.J. & Montero de Espinosa F., 1988; Topolov V.Yu. et al., 2006; Kerimov M.K. et al., 2005, 2007, 2009, 2011; Kurbanov M.A. et al., 2009, 2011; Ploss B. et al., 2005]. Along with this, it should be noted that also numerous semiconductive and ferroelectric materials with various properties are as inorganic phase of composites. Such combination of composite components properties allow to create both microactive and nanoactive dielectrics. Created such kind the micro-, nanocomposites and their hybrid have properties not inherent in organic and inorganic phases separately.

Really, polymer piezo- and pyroelements have low piezo- and pyrocoefficients owing to low value of stable dipole orientational polarization as in case of ferroelectric materials. They have low dielectric constants $2-15$ and their low piezo- and pyrocoefficients don't give a large gain in sensitivity to external actions. The composites of polymer-ferroelectric type have positive properties of ferroelectric materials and polymers, and can have large a piezo- and pyrosensitivity. Ferroelectric materials have more thermal stability than polymer materials, but their parameters are low owing to high electric permeability. The thermal stability of polymer piezo-, pyroelectric and electric materials is low, despite there are traps with enough high concentrations, stable remanent orientational polarization, higher value of electret potential difference and better dielectric properties in these materials.

It is known, that polymer electrets, piezo- and pyroelements with relatively high electrophysical and electromechanical characteristics are produced mainly from fluorine-containing high molecular compounds [Kerimov M.K., 2009; Sessler G.M., 1980]. But, simple and more technological thermoplastic polymers of polyolefine family, for example, polyethylene and polypropylene, have very low electret, piezo- and pyroelectric characteristics. So, they aren't used widely in practice, though also they have high electric and mechanic properties.

One of main way of development of the stable piezo-, pyroelectric and electret materials is a creation of physicochemical basis of composite materials based on the polyolefines with various organic and inorganic fillers.

The perspective direction using composite polymer dielectrics is a development on their basis flexible nonlinear elements – resistors, varistors, piezoresistors and thermoresistors. It is known, that for obtaining nonlinear elements, particularly varistors and resistors, from polycrystal materials the below conditions are needed:

- the element must consist of minimum two phases – crystalline and amorphous;
- the potential barrier must form on the boundary of these phases;
- the element must have bipolar conductivity and symmetric voltage-current characteristic;

- the energy gap width of dielectric and semiconductive phases must differ as far as possible for aim of obtaining high potential barrier on the interface.

In composite materials of polymer-inorganic phase abovementioned demands are satisfied efficiently. In addition to these demands in composite materials the potential barrier with large width is formed due to noticeable difference of components density on the interface. Finally, this allows more effectively regulating the parameters of potential barrier and composite nonlinear element.

As it was noted, one of perspective directions using composite active materials is a performance on their basis the film flexible posistors that is the resistors with a positive temperature resistance coefficient. As known, the posistors are mainly created on the basis of ferrosemiconductive materials, particularly, barium titanate the specific resistance of which is decreased by doping of impurities of rare-earth elements of lanthanum, cerium etc. The formation of posistor effect in this ferroceramic is connected with the tetragonal-cubic phase transition when it is occurs an increasing of barrier width on the boundary of ceramic grains. It is accompanied by sharp increasing of electric resistance and decreasing of dielectric constant.

By synthesis of ferrosemiconductive posistors on the basis of barium titanate we need to accept a quite a number of disadvantages: a high temperature sintering, a narrow concentration interval of doped admixtures, complexity of technology due to using superpurity raw material. Posistor effect in composites based on the crystallizable polymers and ferroelectric particles is caused by presence of barrier layer on the boundary of ferroelectric particles the height of which is defined by dielectric, electronic, electrophysical and thermophysical parameters of components, and also by supramolecular structure of polymer matrix after its dispersion.

Dielectric and thermophysical characteristics of posistor composites are defined by both properties of inorganic dispersing agents and polymer matrix, and also by temperature-time regime of crystallization of the polymer composites in whole. It gives a possibility to regulate the formation of the posistor effect in composites in wide temperature interval, also to develop the posistors with stepless control of temperature of the posistor maximum occurrence.

It should be noted, that the operation of composite transducers in various conditions and regimes has revealed their advantages and disadvantages, and targeted at their improving. The reliability and stability of developed transducers is much depended from right solution of this problem. For expansion of range and conditions of composite transducers applications we need to define mechanical and electrical strength properties of their active dielectrics. It is one of the most important operating indexes of composite transducers in every range of their application. For example, when a shock wave passes through electret, pyro- and piezoelectric transducers, the mechanical stress and electric field are appeared in these materials, which promote an accelerated damage of these elements. It is known also, that when electrothermopolarization the composite material is hold long time in electric field at various temperatures, and in some cases under the simultaneous action of electric, mechanical and temperature fields.

2. Obtaining active composites and methods of their properties investigation

2.1 Choice components, obtaining homogeneous mixtures and composites on their basis

The process of obtaining some composites includes at least three stages: 1) preparation and choice initial components; 2) mixing components; 3) obtaining composite material from

components of homogeneous mixture. A choice component of the composite and method for obtaining a composite active material is dictated by the set of properties that the final material should possess. In connection with this, when development of composites the polymer phases should meet next demands: easy processing, high plasticity and mechanical strength, heightened dielectric constant and electric strength, minimal dielectric loss.

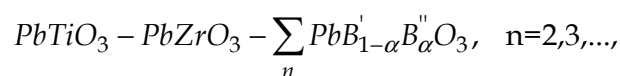
The assessment of specific demands of occurrence processes of the internal stress and relaxation of structures when obtaining and processing composites based on the selected matrix is not less important. The melting temperature must be enough high for that the structure and charge state of obtaining composites aren't damaged by electrothermoprocessing. The glass transition temperature must be low for providing stable relaxing properties defined the temperature interval of reproducibility of the composite parameters.

The analysis of thermophysical, electrical and physical-mechanical properties of polymers showed that the thermoplastic nonpolar polymers of polyolefine series and the fluorocarbon polar polymers (high density polyethylene HDPE, low density polyethylene LDPE, polypropylene PP, polyvinylidene fluoride PVDF, copolymer vinylidene fluoride with tetrafluorethylene, polyvinylchloride PVC and polytrifluoethylene) are suitable under abovementioned demands. At those of polymer matrix, in point of view of the pyro- and piezoelectric composites, the determinative factor is high values of the dielectric constant and specific volume resistance; but in point of view of electret composites the matrix must possess deep centers of charges capture. Besides, it should note, that already an industry developed production of thermoplastic polymers of polyolefine series and the fluorocarbon polymers. It is a key factor in economic point of view for development of transducers based on the polymer composites. Pointed polymers are distinguishing their physical-mechanical properties and structures. For example, polyethylene and polypropylene are nonpolar polymers with low values of dielectric constant and high volume resistance. But fluorocarbon polymers are polar polymers with high values of dielectric constants, but low volume resistance. Fluorine-containing polymers possess not bad piezo- and pyroelectric, electret and light-sensitive properties. It should note that by changing of isothermal regimes of moulding and temperature-time conditions of crystallization we easily can vary of supramolecular structure of pointed polymers [Sessler G.M., 1980; Marikhin V.A. & Myasnikova L.R., 1977].

The demands to active elements are differentiated by effects waited from composite materials. As active fillers the most effective ferro piezoelectric and ceramic semiconductors with various structures were used for electret, piezo- and pyroelectric, posistor and varistor composites.

The investigations of piezoceramic materials brought into the obtaining of effective piezoelectrics and pyroelectrics based on the PZT. Then, on the basis of PZT the more effective piezoceramic materials were produced by doping of ternary oxides [Fesenko E. G., 1983; Lines M.E. & Glass A.M., 1977; Burfoot J.C. & Taylor G.W., 1979; Rez I.S. and Poplavko Yu.M., 1989]. In connecting of this, as fillers (inorganic dispersing agents) the multicomponent piezoceramic materials of PZT family were used. As will be shown below, obtained on the basis of various polymer dielectrics and multicomponent ferro piezoelectrics the composite materials are more effective and possess high electret, piezo- and pyroelectric properties in comparison with composites having double component PZT as dispersing agent. Used multicomponent ferro piezoelectric materials had rhombohedral (Re), tetragonal (T) and compound (heterogeneous Re+T) structures. At this a morphotropy range is considered as important reference point when choice an active phase (dispersing agents)

dividing system on rhombohedral and tetragonal phases. So, used main piezoceramic materials are solid ferroactive solutions of multicomponent systems of type:



which possess various symmetry, piezo-, pyroelectric characteristics and dielectric properties in dependence of position relative to morphotropy range.

By development of piezoresistive, posistor, varistor, photoresistor, photovoltaic, photoelectret and nanostructured systems, the simple semiconductors of Ge, Si, Se, GaSe, CdS, ZnS, ferrocene, monochalkogenide and one-and-a-half chalcogenide of rare-earth elements were used. A choosing of their as active phase is connected with that some of them were recommended themselves as effective materials for sensors of various purposes.

Next technological operation is a mechanical mixing of prepared powder-like thermoplastic polymers with powder-like inorganic dispersing agents. The technology of such mixing is known well. It includes a stage of preliminary dry mixing of powder-like components (polymer and active phase) and a stage of homogenizing in a powder-like state and then in a melt. It should be noted, when doping filler, a viscosity of polymer melt increases, and this complicates its processing in a product by high effective methods of extrusion and press molding. The limiting level of filling is determined by two indications: permissible changing of properties of the material and its rheological characteristics.

As far as, when development of active elements it is needed to obtain composites with volume contents of particles of the dispersing agents till 80%, an application of modern methods of extrusion and press molding was became practically impossible. Really, in according with published articles, and also carried out experiments, mixing granulated equipment, extruders for forming of product are used only for composites contented 25-35% vol. particles of the dispersing agents. But even in case of less content of filler, an extrusion and calendering don't provide obtaining nondefect on particles distribution composites. In this, the method of hot pressing of preliminarily carefully homogenized mixture of composite component is most acceptable. This method becomes irreplaceable due to possibility of carrying out thermoprocessing and even polarization in single technological cycle. In experimental part it will be shown, that such processing appreciable increases an efficiency of obtained active materials.

So, the method of obtaining of a composite material is consisted in the following: 1) a homogeneous mixture is obtained from powder polymers and dispersing agents (active phase) in a mechanical mixer (a laboratory ball mill); 2) pellets are obtained from mixture by cold pressing; 3) during some time, pellets are hold at the melt temperature under a small pressure; 4) at this temperature, a pressure is slowly increased till pressing pressure and then sample is hold over time of pressing; 5) then a pressure is removed and a sample is cooled in water with ice, or in liquid nitrogen, or slowly cooled under a pressure.

Taking into account, that generally, thermoplastic polymers are used as polymer matrix of composites, a pressure and temperature of pressing of their composite are little differed, and change into 15÷20 MPa и 443÷550 K intervals, respectively. When choosing a pressure and a temperature of composite pressing it is need to take into account the temperature of decomposition of a polymer matrix and mechanical destruction particles of the dispersing agents under the mechanical stress arising during pressing.

2.2 Investigation method of charge state of composites-thermoactivated spectroscopy

The methods of thermoactivated current spectroscopy are widely applied for investigations of electrophysical properties and charge state of semiconductive, dielectric and ferroelectric materials. The basis of this method is that when a linear changing of temperature an object transits from non-equilibrium state to new thermodynamic equilibrium one. One of the methods of thermoactivated current spectroscopy is a method of thermostimulated depolarization (TSD). It consists of next: studied dielectric is preliminary polarized under the action of intense electric field in a combination of other actions (heat, visible or UV lighting, radiation, mechanical stress). At this, polarization can occur on next ways: orientation of polar molecules or domains along of field; a displacement (migration) of free charge carriers on a macrodistance with following locking on the traps; an injection of charge carriers from electrodes and following their capture by traps; a displacement of free charge carriers on a microdistance with their capture by traps and an accumulation of charges on the interphase boundary in polycrystalline and composite materials.

Polarized dielectric is cooled under the field till less temperature, and then it is heated on the certain law in short-circuited state. As at this, charge carriers, dipoles and domains, change their positions in space, then, in common case, there is a depolarized current in an external circuit. There is a changing the value of induced charge on electrodes. A density of depolarized current can be describe by formula [Sessler G.M., 1980]

$$j(t) = q \cdot \mu \cdot n(t, x) \cdot F(t, x) + \lambda(t) \cdot F(t, x) + \frac{\partial}{\partial t} [\epsilon \epsilon_0 \cdot F(t, x) + P(t)]$$

where, q , μ , n are a charge, mobility and concentration of free polarized charge, F is an intensity of internal electric field, $\lambda(t)$ is a equilibrium conductivity of sample, ϵ is a dielectric constant of sample, $P(t)$ is a relaxation polarization of sample.

There is in the expression, the first term describes nonequilibrium conductivity current; the second one describes a equilibrium conductivity current; the third one describes a displacement current due to relaxation of macroscopic heterogeneous and homogeneous polarization. Electrodes with the help of special cable are connected to electrometer for registration of depolarized current. The control of sample's temperature on a linear law is carried out with the help of the special regulator of temperature.

The method of thermoactivated current spectroscopy is effective for investigation of electret, piezo- and pyroelectric properties of composites as far as it allows to define the value of stabilized charge and domain-orientational polarization formulated in the processes of electrothermopolarization. For investigation of TSD of composites in temperature range of 77÷520K, the special set, regulator of temperature, was developed. It allows to investigate TSD in the regime of fractional heat, and also under the simultaneous action of a mechanical stress on the composite.

On the TSD curves the parameters of dipoles, electron and ionic centers of captures of the charge carriers can be determined. These parameters are: activation energy, frequency factor and concentration. The most simply these parameters are determined by TSD curves received in the regime of linearly heat of composites, contented one kind of electrical active centers. There are suggested many various methods of determine of activation energy of charge relaxation on TSD current curves. Particularly, it can be determined on temperature position of maximums of TSD current, by the method of a heat rate variation, on the character points of TSD curve [Sessler G.M., 1980].

Piezoelectrical and electromechanical properties of composites are measured by quasi-static method of resonance and antiresonance, and in dynamic regime using acoustic equipments of Bruel & Kjaer firm.

Also, the remanent reorientation polarization P_r of the composites was determined from their thermally stimulated depolarization curves. The same technique was used to determine the pyroelectric coefficient $\gamma(\Delta P_r/\Delta T)$, which is a measure of the pyroelectric activity of the composites. The current gradually decreases in sequential heating-cooling cycles and is reproduced in magnitude beginning with the seventh to eleventh cycle. The reproducible current was approximately ten times lower than the current measured in the first heating cycle. Therefore, the thermally stimulated current contains the reproducible and irreproducible components. The irreproducible component is associated with the release of charge carriers from shallow traps at the sample surface and in the polymer phase. The reproducible current component is determined by the change in the remanent reorientation polarization of the pyroelectric ceramic phase as a function of temperature. It should be noted that a symmetric dependence of the pyroelectric current in a heating-cooling cycle is observed only after the reproducible thermally stimulated current is attained. This is one of the indications of the pyroelectric effect in materials, in particular, polymer-pyroelectric ceramic composites. In this case, the pyroelectric current reversed direction, whereas the current magnitude remains identical to that observed upon heating of the sample. Upon change in sign, the current of thermally stimulated depolarization undercooling initially passes through zero due to the sharp increase in the relaxation time and then rapidly increases. The symmetric dependence of the pyroelectric current in the heating-cooling cycle is ensured by the quantity dP/dT . After the symmetric dependence was attained, the total thermally stimulated depolarization curves were measured and the remanent reorientation polarization in the composites was determined from the areas under these curves.

Electret potential difference and electret charge were determined by using TSD methods and registration of induction current.

3. Composite matrix piezo- and pyroelectric materials

The composites are widely applied almost in all fields of technology and constitute the background of the most natural materials. In this connection a lot of works are devoted to their fabrication technology and studying of their macroscopic characteristics [Sessler G.M., 1980; Kerimov M.K., 2005, 2007, 2009; Kurbanov M.A., 2009, 2011; Topolov V.Yu. et al. 2006; Smay J.E., 2002; Zhang Q.M. & Geng, 1994; Mamedov G. et al, 2010], significantly, of the practical directionality. As far as the structures and features of composites are extremely various, the general approach for explanation of their properties the formation practically is absent.

The most common representation of composites feature formation is based on account of characteristics of the constituents. In this case the geometry (size, shape) and their relative position are taken into account. The interaction between the phases is considered negligible, i.e. contributions of phase properties to integral characteristics of composites are taken additive. By this approach there is no necessity in separation of composite material physics. It follows also from adopted definition of composites as the heterogeneous system, obtained from two or more components with conservation of individual properties each of them. However, one cannot neglect the interaction between the phases formed the composites as far as it becomes decisive in formation of their properties for many cases. The obvious example of the impossibility of determination of the integral features of composites starting from additivity of the contributions of the phases is a system consisted of sequentially connected phases between which $p-n$ junction is formed.

Below we shall make an attempt to show the necessity of accounting of the interface interaction, the electron states of phase interface and charge stabilizations init formation of the composite properties on example of disordered polymer-piezoelectric system.

High density and low density polyethylene (HDPE and LDPE), polypropylene (PP), polyvinylidene fluoride (PVDF) are used as a matrix of composites. Multicomponent piezoceramics of lead-zirconate-titanate family of PCR-piezoceramics Rostov type are used as active filler. The USA analogues of used PCR piezoceramics are presented in table 1.

Used PCR-piezoceramics Rostov type and its analogous in brackets	PCR-1 (PZT-5A)	PCR-3M (PZT-7A)	PCR -5 (PZT-75)	PCR -7M (PZT-5H)	PCR -8 (PZT-8)
${}^2d_{33}/\epsilon_0\epsilon_r$, [Vm/N]	$33.0 \cdot 10^{-3}$	$24.0 \cdot 10^{-3}$	$29.0 \cdot 10^{-3}$	$15.8 \cdot 10^{-3}$	$23.2 \cdot 10^{-3}$

Table 1. The comparison of the piezoelectric properties of the composites based on the same polymer with different piezoelectric fillers.

Samples are obtained based on the homogeneous mixture polymer-piezoparticles by hot pressing method. Diameter of the piezoparticles was changed from 63 to 100 mkm. Thickness of samples was varied from 80 to 200 mkm. Piezocoefficient (d_{ij}) of composites was measured in the quasistatic condition with error not more 8%. Volume fraction of piezophase was changed from 40 to 70%. Polarization of composites was brought off in simultaneously action of constant electric field and temperature. Magnitudes of electric intensity (E_p) and temperature (T_p) of polarization were limited by electric strength of breakdown and melting temperature of samples.

Let's consider the role of polarization processes taking place in a polymer matrix and on polymer-piezoelectric interfaces on the basis of following experimentally stated facts:

1. The dependences of piezocoefficient of HDPE+50%vol.PCR-1 composites vs polarization electric fields E_p , and temperature T_p are shown in fig.1a,b. With increasing of E_p and T_p the composite piezocoefficient (d_{33}) is increased, passes via maximum and then is decreased. As far as the temperatures and electric field intensities of polarization is smaller than Curie temperature of piezophase and composites electric breakdown intensity correspondingly, then these dependencies mustn't have a maximum.

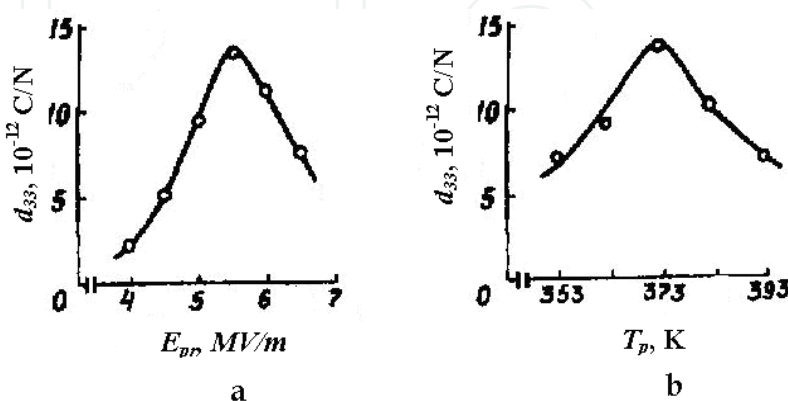


Fig. 1. The dependences of piezocoefficient of HDPE+50%vol.PCR-1 composites vs a) polarization electric fields E_p at $T_p=373$ K; and b) vs temperature T_p at $E_p=5,5$ MV/m. The sizes of piezoparticles are 63 mkm.

2. A comparison of d_{33} values of the composites on the base of the low and high-density polyethylene and polypropylene with the same piezofiller (fig.2) indicates that their piezoelectric coefficient corresponding to the optimum polarization conditions are significantly distinguished.

A theoretical consideration of two phase system based on a polymer dielectric dispersed by piezoelectric particles uniformly distributed in volume, gives [Furukawa T. et al., 1976, 1979; Jamada T. et al., 1982; Wede H. Et al., 1986]

$$d_{33} = F \cdot \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2 + F(\varepsilon_1 - \varepsilon_2)} \cdot \frac{5C_2^2 d_{33}}{3C_1 + 2C_2 - 3F(C_1 - C_2)}, \quad (1)$$

where ε_1 and ε_2 are dielectric constants of the polymer matrix (phase I) and piezoceramics (phase II), accordingly, C_1 and C_2 are appropriate flexibleity modules. F is the volume fraction of piezofiller; $^2d_{33}$ is a piezocoefficient of piezofiller.

With taking into account $\varepsilon_1 \gg \varepsilon_2$ and $C_2 \gg C_1$ one obtains

$$d_{33} = \frac{15F}{(1-F)(2+3F)} \cdot \frac{^2d_{33}}{\varepsilon_1} \varepsilon_1 \quad (2)$$

It is seen, that the piezocoefficient of composite is proportional to ε_1 of polymer phase and piezoceramics sensitivity ($^2d_{33}/\varepsilon_2$). Thus, this experimental fact has no explanation within the scope of theory, since ε for the polymers of the polyolefin chain is the same.

3. The comparison of the piezoelectric properties of the composites based on the same polymer with different piezoelectric fillers (table 1) also shows that the piezocoefficients of the composites (fig.3) are not proportional to the ratio $^2d_{33}/\varepsilon_2$ as it is predicted by theory.

4. It is seen from preceding results that for the optimal polarization the composites have significant piezocoefficient that points to high polarization of piezophase. Nevertheless the effective field E acted on isolated spherical piezoparticles in composite is defined according to Frelich theory with taking into account $\varepsilon_1 \ll \varepsilon_2$ by relation

$$E = \frac{3(1+2F)}{1-F} \cdot \frac{\varepsilon_1}{\varepsilon_2} \cdot E_p \quad (3)$$

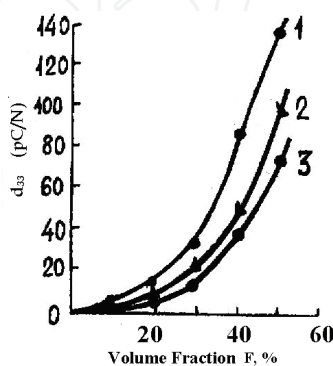


Fig. 2. The composite piezocoefficient values on the base of the low and high-density polyethylene and polypropylene with the same piezofiller: 1-PP+PCR-3M; 2-LDPE+PCR-3M; HDPE+PCR-3M. The sizes of piezoparticles are 63 mkm.

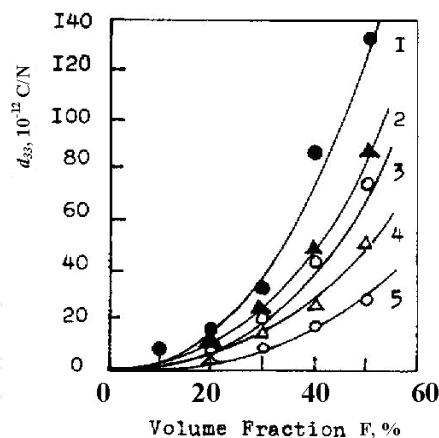


Fig. 3. Piezocoefficient d_{33} as a function of piezoceramic volume fraction for composites on the basis of polypropylene and piezoceramics with different ${}^2d_{33}/\epsilon_2$: 1) PP/PCR-3M, ${}^2d_{33}/\epsilon_2=0.024$ for PCR-3M; 2) PP/PCR-5, ${}^2d_{33}/\epsilon_2=0.029$ for PCR-5; 3) PP/PCR-7M, ${}^2d_{33}/\epsilon_2=0.0158$ for PCR-7M; 4) PP/PCR-1, ${}^2d_{33}/\epsilon_2=0.033$ for PCR-1; 5) PP/PCR-8, ${}^2d_{33}/\epsilon_2=0.24$ for PCR-8. The sizes of piezoparticles are 63 mkm.

It is seen, that the field intensity per of piezoparticles during thermopolarization much smaller than the applied field of polarization E_p and coercive field of piezoceramic and consequently the piezoparticles must not be efficiently polarized.

The attempts were made to explain the significant distinctions between the experimental data and theoretical calculations with taking into account the third phase supposedly arising as a result of the interaction of the piezoparticles and polymer [Hiroyoshi Ueda et. al., 1986; Furukawa T. Et al., 1976, 1979; Wede H. Et.al. 1986; Jamada T. Et al. 1982]. However, the use of such model leads to no reasonable values for parameters of the intermediate third phase, considered as fitted one for the agreement of the theory and experiment.

Numerous experimental results [Topolov V.Yu. et al., 2006; Zhang Q.M. & Geng X., 1994; Kerimov M.K. et al. 2005, 2007, 2009, 2011; Kurbanov M.A. et al., 2009, 2011] for the composites based on piezoceramics and polymers with the various structures polarities verify the fact listed above and point to necessity for different approach in explanation of the piezoelectric properties formation of composites. In particular, all these facts may be explained if one takes into account an interconnection of charge accumulation processes in polymer matrix and piezophase polarization of composite.

A charge state of the composites has been investigated by the thermostimulated depolarization method (TSD). In fig.4 the typical TSD spectra of composites based on HDPE and PZT-19 are shows. These are two maximums on spectra. The first, low temperature one is coincides with the TSD maximum of pure polymer. Activation energy of the first TSD maximum of the composite is close in a magnitude to the activation energy of TSD maximum of a base polymer.

One can come to conclusion that the first maximum of TSD spectrum is caused by liberation of charge carriers from the traps in polymer. The second maximum of TSD current of a composite is connected with a relaxation of charge captured by traps with high activation energy. One can suppose that these traps are located in polymer phase the structure of which is formed under the influence of piezoparticles surface, that is, in boundary layer of polymer near the particles of the piezoceramic.

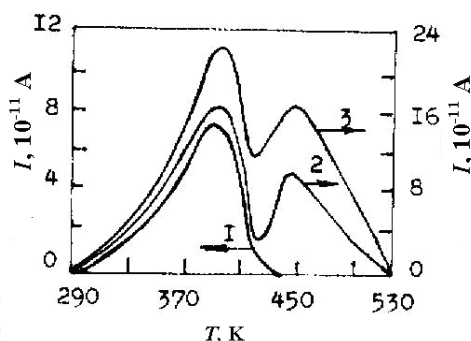


Fig. 4. TSD spectra of composites based on HDPE and PZT-19. 1-HDPE; 2-HDPE+30% vol.PZT-19; 3-HDPE+50% vol.PZT-19. $E_p=5.5$ MV/m; $T_p=373$ K. Polarization time – 0.5 hour.

A role of the stabilized charge on the polymer-piezoceramic interface in formation of the piezoelectric properties of the composites is verified by following experimental facts:

1. The dependencies of the total charge Q , charges Q_1 and Q_2 corresponding to the first and second TSD maximum vs E_p and T_p (fig.5) for PP+50%PZT-19 and content of the piezofiller (fig.6) have the same form as the dependencies d_{33} vs these parameters (fig.1,2,3).

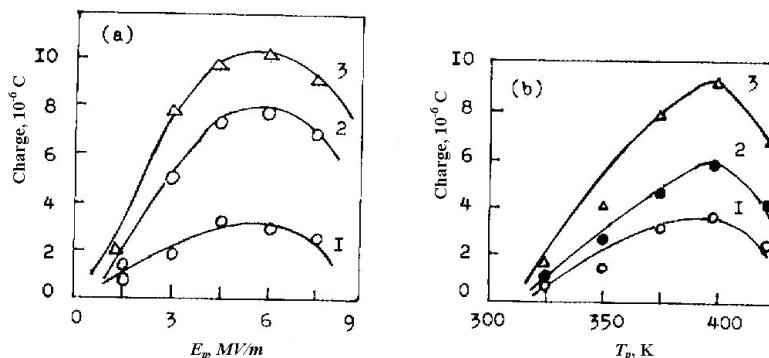


Fig. 5. The dependencies of the total charge Q , charges Q_1 and Q_2 corresponding to the first and second TSD maximum vs E_p and T_p for PP+50%PZT-19. a) 1- $Q=f(E_p)$; 2- $Q_1=f(E_p)$; 3- $Q_2=f(E_p)$. b) 1- $Q=f(T_p)$; 2- $Q_1=f(T_p)$; 3- $Q_2=f(T_p)$.

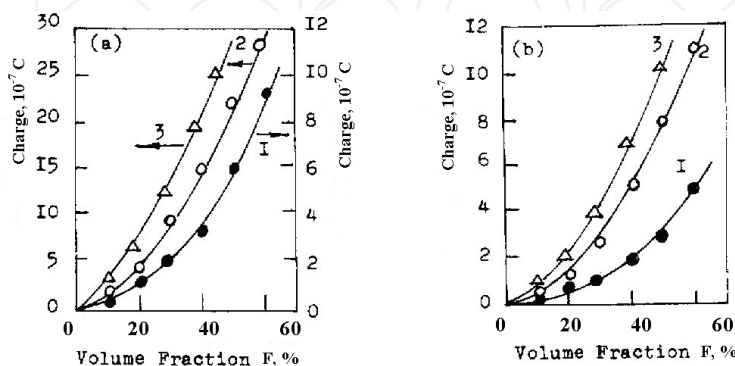


Fig. 6. a) Total charge Q and b) charge corresponding to the second maximum Q_2 of TSD spectra as function of piezoceramic volume fraction. 1) HDPE/PZT-19; 2) PP/PZT-19; 3) LDPE/PZT-19.

2. For determination of this bond we use dependences of d_{33}/Q , d_{33}/Q_2 , and d_{33} on the Q и Q_2 (fig. 7). It is shown, for all contents of piezophase d_{33}/Q_2 is approximately equal. But with increasing F , d_{33}/Q and d_{33}/Q_1 are changed by complicated manner (fig. 7a). Received for various contents of piezophase the dependence of Q_2 on d_{33} is direct proportional, but the dependence of Q on d_{33} has not direct behavior (fig. 7b). Analogous results are received for another composites (fig. 8 a,b): PP-50% vol.PZT-19. From this we can conclude, that a value of piezocoefficient of investigated composites is well correlated with value of charge corresponded to second maximum of TSD spectrum. Such dependencies is not observed for the charges Q , Q_1 and d_{33} (fig. 7,8).

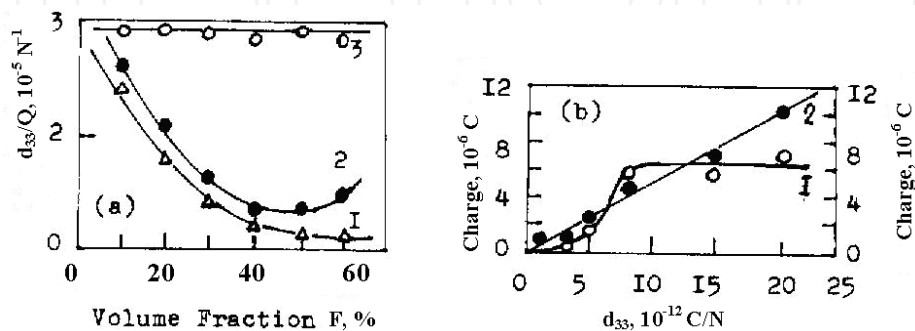


Fig. 7. a) Dependences of d_{33}/Q (1), d_{33}/Q_1 (2) and d_{33}/Q_2 (3) of HDPE-PZT-19 on F . Q - full charge, Q_1 - charge of the first maximum of TSD spectrum, Q_2 - charge of the second maximum of TSD spectrum. b) Dependences Q (1) and Q_2 (2) on d_{33} of HDPE-PZT-19 composite.

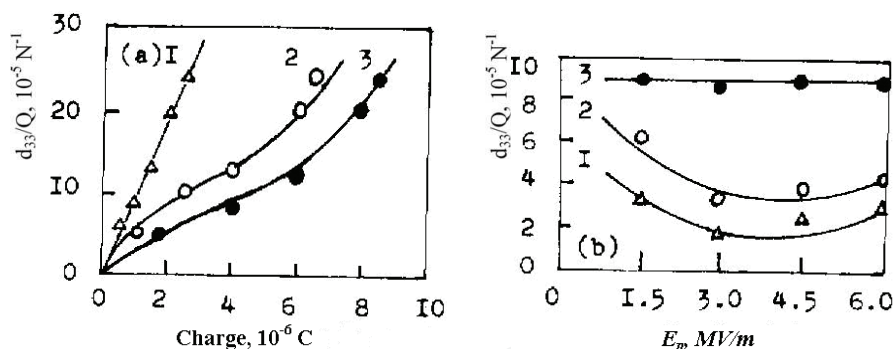


Fig. 8. a) Dependence d_{33} on Q_2 (1), Q_1 (2) and Q (3) for various E_p and $T_p=273K$. b) Dependence d_{33}/Q (1), d_{33}/Q_1 (2) and d_{33}/Q_2 (3) on E_p of PP-50% vol.PZT-19 composite.

3. The values of Q_2/Q_2 and d_{33}/d_{33} practically is constant (fig.9), but Q/Q and Q_1/Q_1 is entirely relaxed (fig.9 and 10) with the heating till temperature of TSD spectrum minimum. Here, Q , Q_1 , Q_2 and d_{33} are value of pointed parameters after first heat of polarized composite. It is shown from fig.10, after the first heat, the first maximum of TSD spectrum disappears and second maximum decreases slightly. After first heat, also a piezocoefficient of composite decreases slightly too.
4. The simultaneous relaxation Q_2 and d_{33} is observed at temperatures beyond second TSD maximum temperature (fig.11).

So that above listed experimental results indicate that the tight binding between the accumulated charges on the phase interface in polymer matrix and piezophase polarization is formed. Such interconnection may be explained on the basis of a simplified model showed in fig. 12.

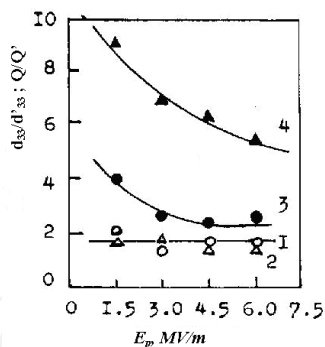


Fig. 9. The dependences of values of d_{33}/d'_{33} (1), Q_2/Q'_2 (2), Q/Q' (3) and Q_1/Q'_1 (4) vs E_p for PP-PZT-19 composite F-5-%; $T_p=393K$.

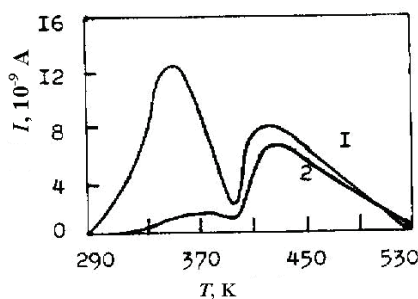


Fig. 10. TSD curves of LDPE-30% vol. PZT-19. 1-at first heating till 413K and cooling till room temperature; 2-at second heating.

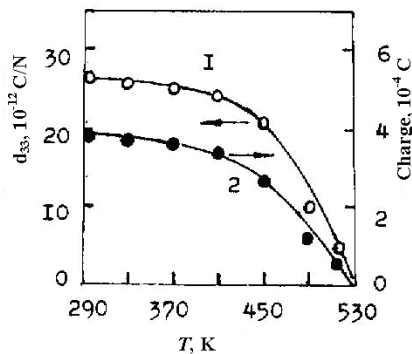


Fig. 11. The dependences of Q_2 and d_{33} vs temperature LDPE-30% vol. PZT-19 composite.

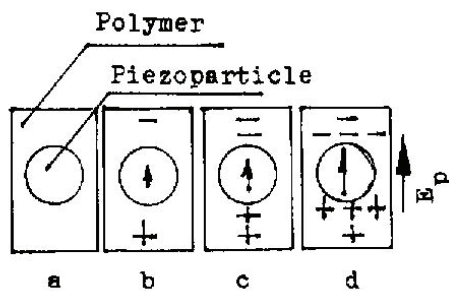


Fig. 12. A simplified model of the accumulated charges on the phase interface in polymer matrix

According to this model the polarization process goes on by following way. At $E_p = 0$ a total polarization of piezoparticles is equal to zero (fig.12a). During electrothermopolarization in the initial moment the charges are injected from electrode to the composite and at the same time insignificant polarization of piezoparticles takes place (fig.12b). This insignificant polarization compensates a fraction of per particle external field in accordance to the dielectric constants and phase conductivities for choosed T_p and E_p . Then, the injected charges drift towards the piezoparticles and are localized on the traps near the phase interface. This leads to the amplification of the local field on a piezoparticles and increase is polarization (fig.12,c).

A formation of quasi-neutral complexes injected charges-oriented domain favors the further injection and drift of the charges towards the piezoparticles and their appropriate to their polarization (fig.12,d). This explains an effectivity of composite polarization. It would seem that process must be continued till a total polarization of the particles. However, in practice a number of facts may prevent it, for instance a deficiency of amount of the deep traps on the interface, a screening of the piezoparticles by accumulated charge and etc.

The efficiency of the piezocomposites polarization becomes dependent on the piezoceramic structure. In fig.13 for example the dependencies of d_{33} and Q on a volume fraction of piezophase of various structures are shown. It is seen, that the magnitude of stabilized charge and the piezocoefficient value are greater in the case of using of the piezoceramic of rhombohedral (R_h) (PCR-3M) structure as a piezofiller compared with the tetragonal (T) structure (PCR-7M) piezoceramic. At the same time the base ceramic have reverse relation of the piecoefficient.

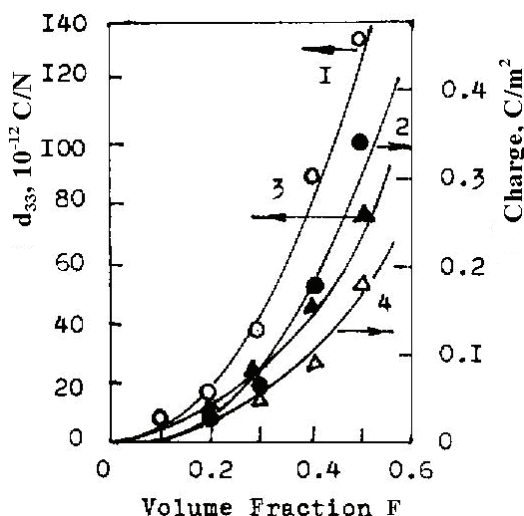


Fig. 13. d_{33} (1,3) and Q_2 (2,4) of composites as a function of piezoceramic volume fraction of different structure. Composites are obtained on the basis of polypropylene. (1,2) for PP-PCR-3M composite; (3,4) for PP-PCR-7M composite. $E_p=3$ MV/m, $T_p=410$ K, $t_p=0.5$ hour.

In [Fesenko E.G. et al., 1983] a high value of the piezocoefficient of tetragonal piezoceramics is associated with a large amount of a dielectric constant ϵ and the known relation is used:

$$d_{ij} = 2Q_s \epsilon_0 \epsilon P_r \quad (4)$$

where, Q_s is the electrostriction coefficient, P_r is an amount of the reorientational polarization of domain different from 180° .

Dielectric constant in composites is significantly smaller than in the piezoceramics because of a low value of ϵ at a polymer phase (table 2). Therefore P_r plays a main role and it is greater in the rhombohedral ceramics. On the other hand in the rhombohedral ceramics a mobility of the domain walls is greater, that in turn leads to increasing of a charge moving to the interphase boundaries. That is a cause of a great magnitude Q_2 .

Thus, the above model interactively explains both the polarization curves and the dependencies $d_{33} = f(E_p, T_p)$, and dependence of the piezocoefficient on the piezofiller structure. An additional verification of a workability of the proposed model one may obtain from calculation of d_{ij} of the composites using the expression (4). Taking into account a major role of the interface charges in piezoparticles polarization it should be used Q_2 instead of P_r in formula (4). A magnitude of Q_s for composites is taken to be equal to its value for a base piezoceramic. Such approach is justified by the fact, that the polarization is concentrated in the piezophase. The calculated quantities d_{33} are illustrated in table 2. It is seen, that a good agreement takes place between the calculated and experimental values of d_{33} . Thus, the experimental data and suggested model demonstrate a significant role of one kind of the interface interaction in the formation of the composites properties. This interaction leads to seemed anomalous dependencies of composite properties on a composition.

Composition	ϵ composition	$Q_r, C/m^2$	$d_{33}, 10^{-12} C/N$ (experiment)	$d_{33}, 10^{-12} C/N$ (calculation)
PVDF+7M; F=50%	95	0.22	65	69.9
PVDF+7M; F=50%	70	0.40	80	92.4
PVDF+7M; F=50%	62	0.56	87	118.4
PVDF+7M; F=50%	102	0.25	135	133.0
PP+7M; F=50%	70	0.02	45	4.6
PP+PZT-2; F=50%	75	0.03	55	6.8
PP+PCR-3M; F=50%	80	0.40	120	100.0
PVDF+ PZT-2; F=50%	86	0.35	120	111.0
PVDF+PCR-3M; F=50%	110	0.45	160	161.5
LDPE+PCR-3M; F=50%	100	0.42	130	139.9
HDPE+PCR-3M; F=50%	70	0.14	76	30.0

Table 2. The calculated quantities d_{33} for various composites.

The amount of the composite piezocoefficients for the certain compositions becomes greater than d_{ij} of both components. If the interface interactions would not play a significant role in the formation of piezoelectric effect, then such maximum must be absent.

In the case, when the interaction between the charges localized in a polymer phase and particle polarization as taking into account, this maximum points to the best polarization of piezophase in a composite compared to a base ceramic. In general case the appearance of maximum on diagrams composition-composite properties shows the significant role of the interaction on the interface. In particular, the above pictured interaction on the interface, that is lead to the formation of the system of oriented domain-localized boundary charge, explains the piezoelectric and electret effects in composites.

In fig. 14 pyroelectric current curves for a composite PVDF-PCR-3M is shown. It should be noted, that the pyroelectric effect in composites becomes greater than in base components.

This is in agreement with the above pictured model, which explains an occurrence of the large reorientation polarization responsible for piezoelectric effect [Lines M.E. & Glass A.M., 1977; Kerimov M.K., 2011]. With the existence of coupling charge-domain system, the occurrence of the stable electret state in the polymer-piezoelectric composites for appropriate proportioning their composition is also explained.

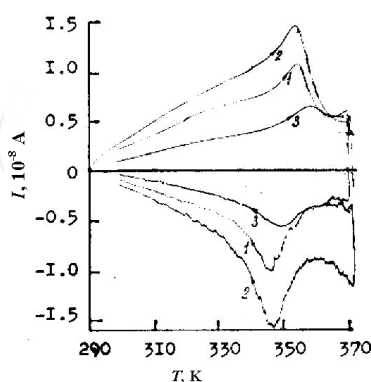


Fig. 14. Curves of pyroelectric current of PVDF-PCR-3M composite: $F=40\%$, $t_p=0.5$ hour, $E_p=3$ MV/m, (1), $T_p=353$ K, (2) $T_p=373$ K, (3) $T_p=353$ K.

A stabilization of charges on the phase interface and their relaxation significantly depends on a structure of polymer on the phase interface. In its turn, this structure is defined by interaction between the polymer chains and piezoparticles surface. In particular, in fig.15 the temperature dependencies of the piezocoefficient and thermal expansion coefficient (α) of composites based on the single matrix and piezoceramic of rhombohedral and tetragonal structures are shown.

It is seen that a temperature decline of the piezocoefficient and a noticeable increase of the thermal expansion coefficient is higher in the case of a piezofiller of the rhombohedral structure.

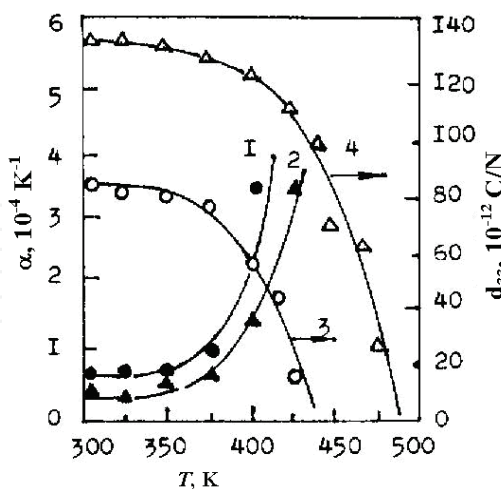


Fig. 15. The temperature dependencies of the piezocoefficient and thermal expansion coefficient (α) of composites based on the single matrix and piezoceramic of rhombohedral and tetragonal structures.

It should be noted, that the piezocoefficient decline is associated with the boundary charges relaxation which, in its turn, is defined by mobility of the polymer chains. It shows that the

interaction of the polymer chains with the piezoparticles surface of rhombohedral structure is stronger. By the same way the dependencies of α vs T are explained also.

A structure and property of near-surface layer affect on a posistor effect in a composite. It is known, that the posistor effect in the piezoceramic is associated with a transition from a ferroelectric phase to paraelectric one [Burfoot J.C. & Taylor G.W., 1979; Lines M.E. & Glass A.M., 1977; Rez I.S. & Poplavko Yu.M., 1989]. In polymers this effect practically is absent. In the composites a significant posistor effect is observed (fig.16). It can not be associated in composites with phase transition in piezoparticles, as far as a temperature of sharp increase of composite resistance is remarkable lower than the piezophase Curie temperature.

The posistor effect in composites is associated with a sharp changing of the potential barrier on the phase interface in melting of ordered phase of a polymer matrix. Such effect is specific only for the composites and may be a basis of a new structure-sensitive method of their investigation. A decrease of mobility of the polymer change both the occurrence temperature and half-width of the posistor peak (fig.16).

It should be noted, that numerous types of interactions are on an interface. The contributions of different interactions naturally will be depending on considered properties. One of principal problems of a compositional material physics must be revelation of major types of interactions on the phase interface and their correct accounting in formation of the corresponding effects. Physics of composite materials must be based on consistent account of contributions of separate type of interactions between phases in the formation of specifically properties of composites.

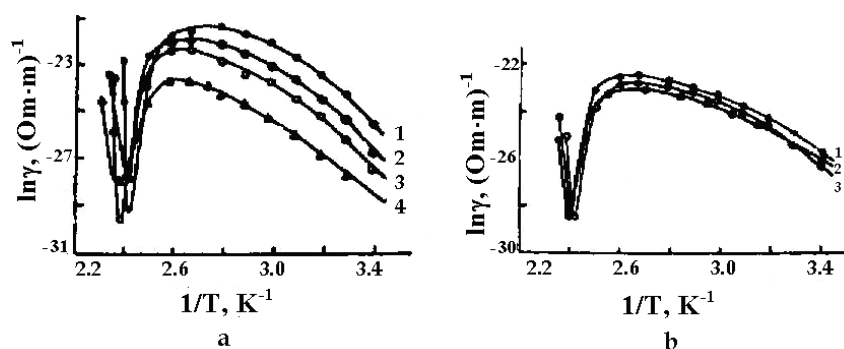


Fig. 16. Observed significant posistor effect in the composites.

Charge states and various interface interactions can be varied by regulation of structure and electrical negativity of components (polymer and ferroelectrical phase), by activation of surface of polymer particles, by doping 3-rd component which increases an adhesion of polymer to ferrophase. Electronic states of polymer-ferroelectric boundary, concentration and activation energy of local levels in quasi-forbidden band of polymer phase are of importance.

We propose a new technological method for varying the structural heterogeneity of polymers and their composites [Kerimov M.K., 2005]. The method is based on the air-discharge plasma-assisted crystallization (electric discharge-enhanced thermal crystallization), which begins at the melting point. We also studied the effect of the electric discharge-enhanced thermal crystallization on the pyroelectric properties of polymer composites.

The electric discharge-enhanced thermal crystallization was carried out as follows. After briefly compressing the composite at the melting point, the upper die was removed from the

surface of the specimen and a special discharge cell was attached to the die. The discharge cell enabled one to activate electric discharges of different intensity in air. An electric discharge was generated in a 4-mm-thick air gap between the teflon plate of the cell and a composite specimen: therefore, a partial discharge was induced [Bagirov M.A., 1972; Kerimov M.K., 2005; Kurbanov M.A., 2009]. A 15-kV sinusoidal electric voltage (50 Hz) was applied to the cell. Using the partial discharge for the electric discharge-enhanced thermal crystallization made it possible to treat the composite surface uniformly without causing noticeable mechanical damage.

Beginning from the melting point of the polymer phase of the composite, the temperature of the electric charge-enhanced plasma-assisted crystallization was changed stepwise (by 10 K over 0.5 h) at the first stage of cooling and then at a rate of 0.25-2 K/min down to the polarization temperature (~373 K) or room temperature. The changes in the structure were studied using the infrared spectra of the polymer phase of a composite. The following polymers were used as a polymer phase: high-density polyethylene (HDPE), polypropylene (PP), and polyvinylidene fluoride (PVDF). As the pyroelectric phase, we used the following pyroelectric ceramics with rhombohedral or tetragonal structure and different Curie temperatures T_c and pyroelectric coefficients γ : PCR-7M ($T_c = 448$ K, $\gamma = 5.6 \times 10^{-4}$ C/m²K), PCR-3M ($T_c = 533$ K, $\gamma = 5 \times 10^{-4}$ C/m²K), and PCR-57 ($T_c = 463$ K, $\gamma = 6 \times 10^{-4}$ C/m²K).

Figure 17 shows the simultaneously recorded spatial (electron-optic converted image) and time (oscillogram) diagrams of the electric-discharge evolution in the air gap between the teflon plate and a composite. As is seen from Fig. 17, the electric discharge in the air gap between the composite and the dielectric is accompanied by separate series of discrete microdischarges. Each voltage pulse on the oscillogram (oscillogram 4 in Fig. 17) corresponds to one series of microdischarges. Each series, in turn, consists of a number of microdischarges generated in different regions of the sample surface. This character of the evolution of partial discharges (microdischarges) enables one to treat the composite surface uniformly and thus carry out effective crystallization of a composite under conditions of a discharge plasma in air with electronegative components.

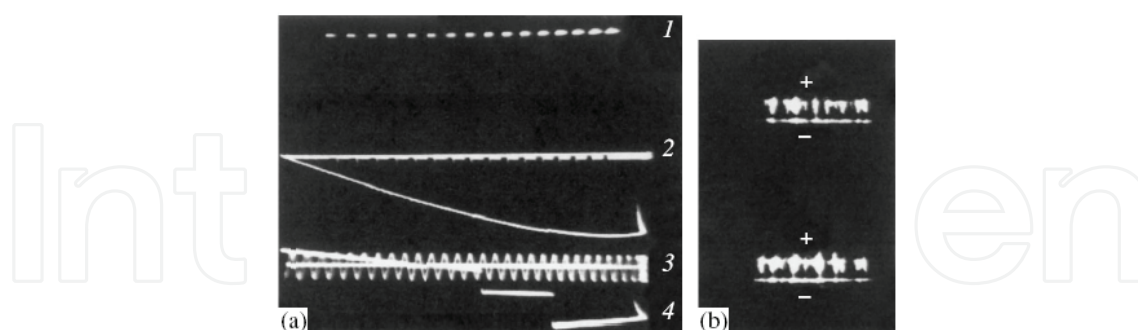


Fig. 17. Simultaneously recorded (a) electrical and (b) optical patterns of the discharge evolution in the air gap between dielectrics. In the oscillogram: (1) gate pulses of the electron-optic converter, (2) voltage change in the test cell, (3) calibrating voltage ($T = 200$ mks), and (4) voltage pulses corresponding to separate series of microdischarges.

Figure 18 shows the changes in the optical density of the bands corresponding to C-O-C, C=O, and OH that appeared in the infrared spectrum of the polymer matrix of the HDPE-PCR-57 composite during its crystallization under the simultaneous action of temperature, electric discharge, and discharge radiation. The results obtained by us show that the

structure of the polymer matrix undergoes substantial changes in the course of electric-discharge crystallization. Indeed, the appearance of C-O-C, C=O, and OH groups in the infrared spectrum indicates changes in the chemical structure of the macromolecules, an enhancement of intermolecular interactions due to the polarity of these groups, and the formation of C-O-C bridges between macromolecules. Clearly, these chemical changes are accompanied by changes in the crystallization conditions and, therefore, in the physical structure of the polymer phase of the composite.

Figure 19 shows the temperature dependence of the pyroelectric current for several successive heating and cooling cycles of the PP-50 vol.% PCR-57 composite. Curve 1 corresponds to the first heating-cooling cycle and represents the nonreproducible part of the pyroelectric current. Curves 2-4 correspond to the reproducible part of the pyroelectric current. The heating (cooling) rate of the given pyroelectric element is 6 K/min. The pyroelectric current reverses direction under switching from heating to cooling, but its value remains the same; in other words, the heating-cooling cycle is characterized by a symmetric temperature-dependence plot of the reproducible part of the pyroelectric current.

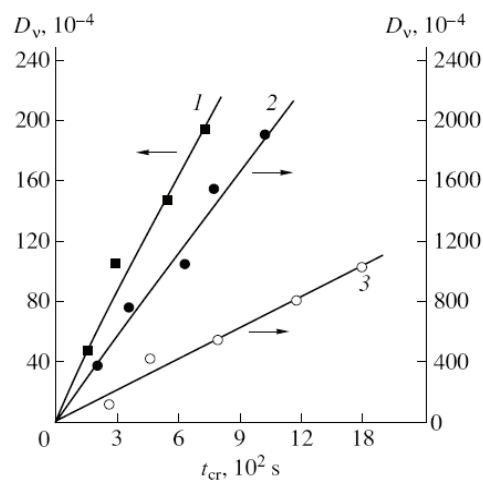


Fig. 18. Variations in the optical density of the bands that arise in the infrared spectrum of the polymer phase of the HDPE + 50 vol % PCR-57 composite during electric discharge-enhanced thermal crystallization. The cooling rate is 2 K/min, $U_p=11.8$ kV, and $\Delta W=1.4 \times 10^{-6}$ J; (1) $\nu=3380$ cm^{-1} , (2) $\nu = 1735$ cm^{-1} (C=O), and (3) $\nu = 1280$ cm^{-1} .

Figure 20 shows the dependence of the pyroelectric coefficient of the PVDF-PCR-57 composite on the volume fraction F of the pyroelectric-ceramic phase. It can be seen that, under the same crystallization conditions, γ increases faster than linearly with F . However, the pyroelectric coefficient of electrothermally crystallized composites is much higher than γ of thermally crystallized pyroelectric elements, all other polarization conditions (E_p , T_p) and the temperature of measurements T being equal.

We also studied the pyroelectric characteristics of a PVDF-based composite filled with particles of a PCR-3M pyroelectric ceramic, which has rhombohedral structure and a relatively high Curie temperature. The pyroelectric ceramics PCR-3M, as well as PCR-57, is characterized by a high pyroelectric coefficient, which, in combination with the low dielectric constant, ensures the high quality factor of this pyroelectric detector, $M_r = \gamma/e = 1.4 \times 10^{-6}$ C/m²K [Fesenko E. G., 1983]. The fact that its pyroelectric coefficient is high at room temperature (Fig. 21) makes this composite promising for pyroelectric elements.

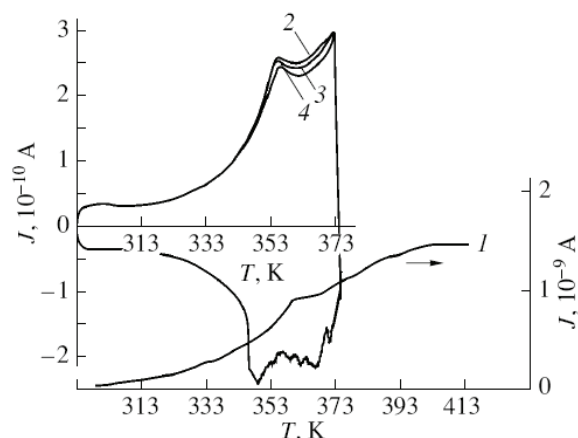


Fig. 19. Dependence of the pyroelectric current on the measuring temperature for the PP - 50 vol % PCR-57 composite. $E_p = 8$ MV/m, $T_p = 373$ K, and $t_p = 1$ h; (1) the nonreproducible part of pyroelectric current and (2-4) the reproducible pyroelectric current.

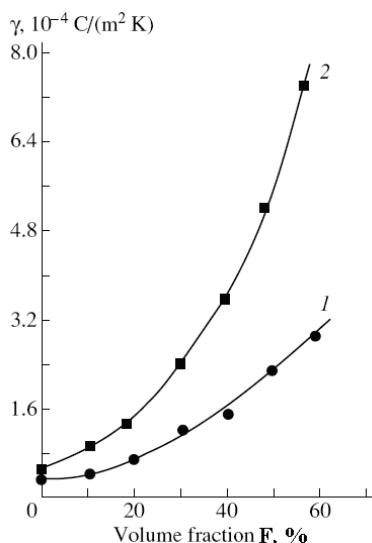


Fig. 20. Dependence of the pyroelectric coefficient γ on the volume fraction of the pyroelectric phase F in the PVDF -50 vol. % PCR-57 composite. $T_p = 373$ K, $E_p = 4$ MV/m. $t_p = 1$ h, and $T = 358$ K: (1) after thermal crystallization and (2) after electric discharge-enhanced thermal crystallization.

It can be seen in Fig.21 that the electric discharge-enhanced thermal crystallization of PVDF-PCR-3M composites results in a significant increase in their pyroelectric coefficients throughout the entire range of measurement temperatures T , including room temperature. Furthermore, the electric discharge-enhanced thermal crystallization significantly shifts the temperature of the onset of an abrupt increase in the value of the pyroelectric coefficient and, therefore, of the pyroelectric current. This experimental result shows that the electric charge-enhanced thermal crystallization increases the interphase interactions, which restrict the mobility of macromolecules of the polymer phase, and causes relaxation of charges on the polymer-pyroelectric-ceramic interface. The measured pyroelectric properties matrix composites that were produced using electric discharge-enhanced plasma-assisted crystallization are shown in the Table 3.

Composites	F, %vol.	T, K	Polarization conditions		γ , $10^{-4} \text{ C/m}^2\text{K}$	
			E_p , MV/m	T_p , K	after thermal crystallization	after electric discharge-enhanced thermal crystallization
PVDF+PCR-7M	50	353	6	353	1.1	4.8
HDPE+PCR-7M	50	353	6	353	0.55	2.7
HDPE+PCR+57	50	353	6	353	0.82	4.2

Table 3. Pyroelectric coefficients of different composites after thermal crystallization and after electric discharge-enhanced thermal crystallization

It is of great interest to consider the kinetics of charge (electron) accumulation at the various stages of crystallization under discharge conditions. Figure 22a shows the space charge generated in an HDPE-PCR-57 composite as a function of the duration of electric discharge-enhanced thermal crystallization. The charge value was found from the depolarization current spectra immediately after electric discharge-enhanced thermal crystallization. The low values of the charge arising at the initial stage of crystallization can be due to electron traps being destroyed under the action of temperature, discharge, and voltage pulses generated during each series of microdischarges and also due to electrons being captured by free radicals of the polymer phase [Vannikov A.V. & Grishina A.D., 1984]. It should be noted that, in ac electric fields, a fraction of the injected charges reappears at the electrode when the polarity is changed. The charges localized in deeper traps can enhance the electric-field intensity in the polymer composite at each air-gap breakdown during the electric discharge-enhanced thermal crystallization. The electron bombardment and the strong local field also initiate the formation of radicals [Bagirov M.A., 1972].

The results obtained allow us to suggest the following mechanism for changing the pyroelectric properties of composites during electric discharge-enhanced thermal crystallization. We believe that, in the course of electrical loading of the composite-gaseous medium-composite system, partial discharges occur and conditions are created for rather complex physicochemical processes in the bulk of the polymer phase caused by electron-ion bombardment, radiation, local heating of the contact between the microdischarge channel and the polymer (Fig. 17b), and active gas-discharge products (O_3 , O, OH, NO). Together, these components of a partial discharge predetermine the specific features of the formation, transformation, and accumulation of free radicals, which account for all structural and energy changes in the polymer phase of the composite. It should be noted that the structural rearrangements that accompany the transition of the polymer from the fluid state to a highly elastic and finally to a glassy state in the course of the crystallization result in an abrupt change in the amplitude of the rotational segmental motion. Furthermore, under the action of temperature and electric discharge-induced plasma, these rearrangements of the structure and the changes in the amplitude of the rotational segmental motion will be significantly different due to electronic, ionic, destructive, and oxidizing processes. For this reason, the conditions of injection, generation, and transfer of charge carriers and their interactions with the macromolecules are changed in the course of electric discharge-enhanced crystallization. Under the action of electron-ion bombardment and discharge radiation, free radicals will form during crystallization, especially in the temperature ranges corresponding to the fluid and highly elastic states. The most probable mechanism consistent with the partial discharge conditions is the mechanism based on discharge radiation ionization of macromolecules

followed by decomposition of the molecular cation (M^+) into a free radical ($R\cdot$) and a cation fragment (R_2^+): $M \rightarrow M^+ + e$; $M^+ \rightarrow R_1^+ + R_2^+$

In ionized macromolecules, the chemical bonds are excited. Therefore, they break relatively easily, and oxidizing processes begin, resulting in the appearance of new local energy levels in the quasigap of the polymer and, therefore, in the formation of additional carrier traps, which is experimentally confirmed by the results shown in Fig. 22. The effective accumulation of carriers at the polymer-pyroelectric-ceramic interfaces and the strong orientational domain polarization of the pyroelectric phase (curves 3, 4 in Fig. 22b) significantly increase the pyroelectric coefficient (curves 1, 2 in Fig. 22b) of the composites produced through electric discharge-enhanced plasma-assisted crystallization.

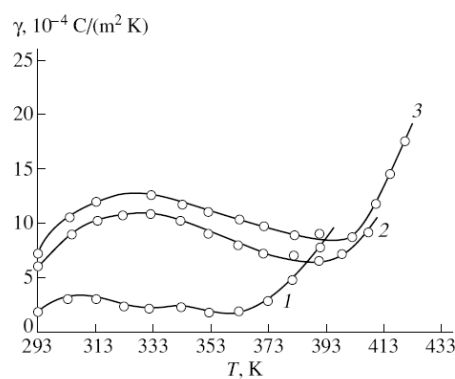


Fig. 21. Dependence of the pyroelectric coefficient γ on the measuring temperature T for the PVDF + 50 vol % PCR-3M composite. $T_p = 373$ K and $t_p = 1$ h; (1) after thermal crystallization ($E_p = 1.5$ MV/m) and (2, 3) after electric discharge-enhanced thermal crystallization at $E_p = 1.5$ and 3 MV/m, respectively.

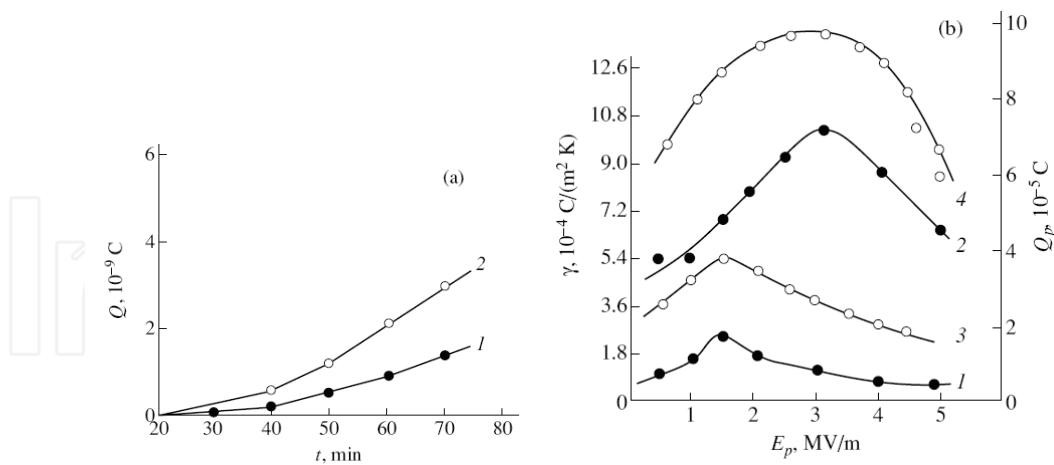


Fig. 22. (a) Dependence of the stabilized charge Q on the cooling duration in the course of electric discharge-enhanced thermal crystallization of the HDPE - 40 vol. % PCR-57 composite. The cooling rate is 1.5 K/min; the treatment voltage U is (1) 16 and (2) 18 kV. (b) Dependence of (1, 2) the pyroelectric coefficient γ and (3, 4) the charge Q_p accumulated during polarization on the electric-field intensity E_p of the PVDF - PCR-3M composite. $T_p = 373$ K, $t_p = 1$ h, and $T = 373$ K; (1, 3) after thermal crystallization and (2, 4) after electric discharge-enhanced thermal crystallization.

The results obtained by us show that the method of electric discharge-enhanced thermal crystallization should be promising for the development of highly efficient active composites. However, these interesting results currently cannot be exhaustively explained, because these studies are at the initial stage. It may be said that the pyroelectric properties of polymer-pyroelectric-ceramic composites produced through electric discharge-enhanced plasma-assisted crystallization are significantly improved and that the concentration of charge carriers accumulated in them during electrothermal polarization increases.

The results obtained enable us to make the important conclusion that, in order to design highly efficient pyroelectric composites based on polymers and pyro-electric ceramics, it is necessary to increase the density of localized states in the quasigap of the polymer phase and at the interphase boundary, which can be achieved using electric discharge-enhanced thermal crystallization of the polymer phase of composites.

4. New class of active materials based on the hybrid of matrix nano- and microferroelectric composites

At present, the matrix system, consisting of polar and nonpolar polymers, dispersed piezoceramic particles, is the most effective electret, pyro- and piezoelectric composites [Vannikov A.V. & Grishina A.D., 1984; Topolov V.Yu. et al. 2006; Kerimov M.K. et al., 2005, 2007, 2009, 2011; Kurbanov M.A. et al., 2009, 2011]. For various purposes the power-intensive and low-power acoustoelectric and electroacoustic transducers are developed based on these composites. Piezoelectric transducers have some advantages and some disadvantages. For example, polymer piezoelectric composites in the mode of receiving acoustic waves (mechanical perturbations) have high piezosensitivity, defined as $g_{ij} = d_{ij} / \epsilon \epsilon_0$, where d_{ij} is a piezoelectric modulus, ϵ is a dielectric constant of piezocomposit element, ϵ_0 is a electrical constant. However, piezoelectric polymer composites in the mode of radiation elastic waves are less effective than the piezoceramic elements because of the relatively low values of electromechanical coupling coefficient K_{ij} , specific acoustic power $(d_{ij} Y)^2$ (Y is Young's modulus), mechanical Q_M and piezoelectric quality factor $K_{ij}^2 \cdot Q_M$, electromechanical efficiency $(K_{ij}^2 / tg \delta)$ and high mechanical compliance S_{11}^E [Rez I.S. & Poplavko Yu.M., 1989; Fesenko E. G. et al. 1983]. In addition to these properties, the frequency sensitivity range of amplitude-frequency characteristics of piezocomposit converters is not very wide, and the value of the output signal decreases appreciably when $f \geq 7$ kHz. The application of piezocomposit elements as powerful sources of radiation elastic waves is very important to create a receiving-transmitting acoustic antenna for detection of submarine objects. However, the low values of electromechanical parameters $(d_{ij}^2 Y_{11}^2, K_{ij}^2 / tg \delta, K_{ij}^2 \cdot Q_M, K_{ij}, Q_M)$ of piezocomposit elements reduce the efficiency of acoustic antennas in the radiation mode.

Physical-mechanical and, consequently, electro-mechanical properties of matrix composites depend on the mobility of the macromolecules of the polymer phase and the interfacial interaction. Therefore, by varying these factors, we can specifically regulate the piezoelectric and electro-mechanical characteristics of composites, making them effective in the manufacture of energy-intensive sources of acoustic waves. Nanotechnology advances help solve this problem by creating a new class of piezoelectric materials by the combination of

polymer composites with nano dimensional dielectric and micro dimensional piezoceramic particles.

We propose a technology for creating piezoelectric composites, combining nano- and micro composites integrated with polymer matrix (a hybrid system). The principle of the development of hybrid nano- and micro composites based on the difference in the temperatures of dissolution and melting regions of the polymer composite phase, whose structure is formed under the influence and not under the influence of the surface of micropiezoelectric particles. Progress in nanotechnology allows us to create power-intensive and low-power piezoelectric transducers. At presents, due to lack of nanoscale piezoceramic particles of different structures, determining the piezoelectric properties of the hybrid matrix of nano- and piezocomposites the main component are microscale piezoelectric particles. From the literature it is known that the piezoceramic material of PZT family have a stable structure and are the most effective piezoelectric material to develop on their basis both power-intensive and low-power converters, in particular, receiving and transmitting antennas, and acoustic sensors [Marikhin V.A. & Myasnikova L.R., 1977; Sessler G.M., 1980; Kerimov M.K. et al. 2009].

We proposed polymeric nano - and microhybrid materials combine the phases responsible for the creation of low-power and power-intensive transducers. Nano particles of barium titanate (BaTiO_3) and quartz of various structures have low stability and the Curie temperature. Therefore, they are ineffective materials to create piezoelectric composites. We offer a hybrid piezoelectric composites using nano-materials, which combine the positive qualities of PZT piezoceramic materials of different structures (tetragonal and rhombohedral) and properties (high Curie temperature, piezoelectric modulus, mechanical quality factor, Young's modulus and high coefficient of electromechanical coupling and electromechanical characteristics).

Tumerous experimental results show that depending on the size of particles of piezo-phase the piezoelectric coefficient and Young's modulus of the composites vary not symbatically. Piezo-coefficient of the composite increases monotonically, and Young's modulus decreases with increasing size of piezoceramic particles. This is the reason for the low value of the specific acoustic power $(d_{ij}Y)^2$, electromechanical coupling coefficient K_{ij} , piezoelectric $K_{ij}^2 \cdot Q_M$ and mechanical Q_M quality factor and the high value of mechanical compliance.

Experiments on the influence of dispersion of piezoceramic fillers on the physical, mechanical and piezoelectric properties of piezocomposites showed that for high piezo-module (d_{ij}) the average particle size of piezoceramic must be within 100-250 microns, and for high Young's modulus and low-compliance - under 50 microns (Fig. 23).

Let us primarily consider the technology of the creation of active centers of clusterization of nanoparticles in the polymer phase of the composites by the performance of their crystallization under the effect of the plasma of an electrical discharge [Kerimov M.K. et al. 2011]. The crystallization of the composites under the plasma of an electric discharge involves heating of the material up to the melting point and keeping it at that temperature for 5–30 min (and, not relieving the effect of the discharge) with further cooling down to the temperature of the crystallization of the polymer phase with a rate from 0.5 to 4 K/min with the aim of the directed changing of the chemical (oxidation) and physical (supramolecular) structures of the polymer matrix. The melting point of the composite was determined by the temperature of the third peak of the spectrum of the thermodepolarization current (Fig. 24, curve 2). The duration of the crystallization t_{kr} was

limited to the saturation of the optical density of the oxygen-containing groups (for example, OH and C=O), which evolved in the IR spectrum of the polymer–piezoceramic composite as a result of the action of the electrical discharge, and changed in the range from 5 to 30 minutes.

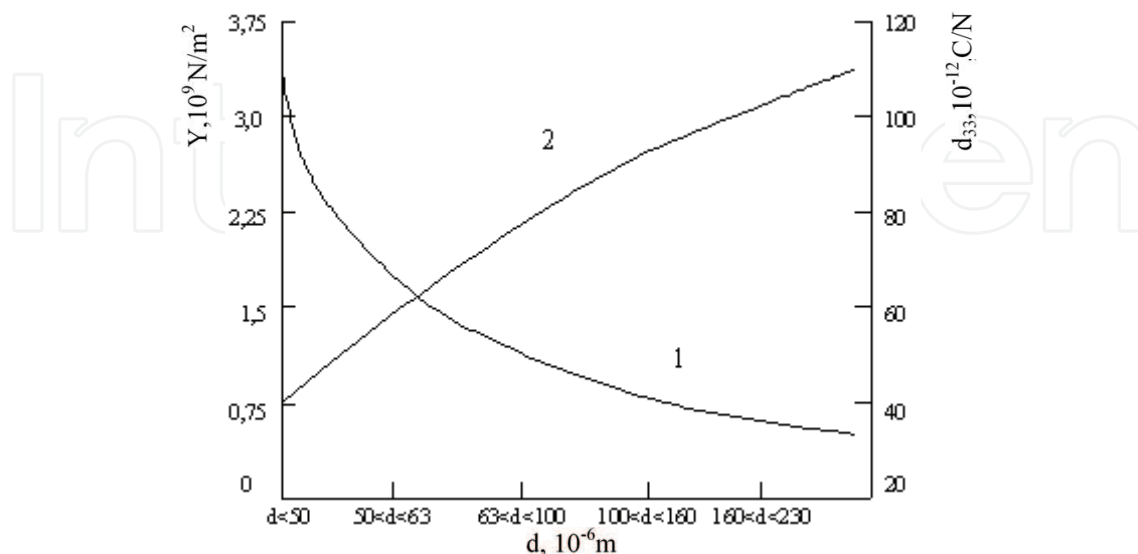


Fig. 23. Change of Young's modulus (curve 1) and piezo-electric coefficient (curve 2) of high-density polyethylene +50% vol. piezoceramic-PZT composite, depending on the size of the piezo-electric particles (piezo-phase).

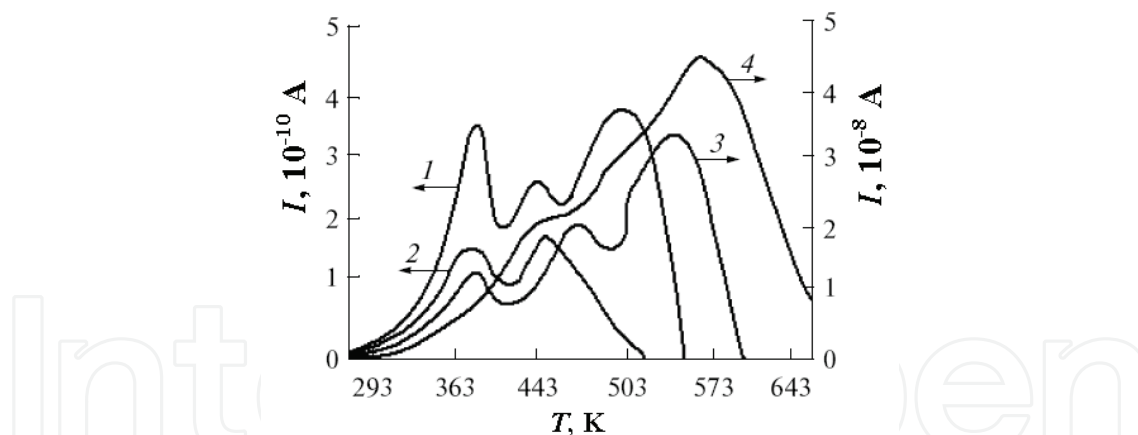


Fig. 24. Spectra of the thermostimulated depolarization current PVDF and the composites on its basis. (1) PVDF; (2) PVDF+50 vol % PZT-5A; (3) PVDF+1 vol % BaTiO₃ + 49.9 vol % PZT-5A, $W= 26.3 \times 10^{-6} \text{ J}$; and (4) PVDF + 1 vol % BaTiO₃ + 49 vol % PZT-5A, $W= 335 \times 10^{-6} \text{ J}$. The conditions of the polarization: the electric field of the polarization $E_p= 3 \times 10^6 \text{ V/m}$, the temperature is $T_p = 413 \text{ K}$, and the time of the polarization is $t_p= 0.5 \text{ h}$.

The experimental results demonstrate that, in the IR-spectrum of the polymer matrix (PVDF) of the composite, after its crystallization under the effect of the plasma of the electrical discharge, new highly polar oxygen-containing groups, C=O and OH, are formed. In Fig. 25, the change in the optical density D of the IR spectrum is given for the mentioned groups in the polymer matrix that crystallized under the conditions of the plasma of an

electrical discharge. It is seen that the change in the optical density D within the time of the crystallization up to 15 min has a linear character. The centers of oxidation can be the seeds for the clusterization of nanoparticles. The next stage of the immobilization is the dissolution of the polymer in toluene. After that, the BaTiO₃ nanoparticles (<50 nm) are introduced into the solution in the range from 0.5 to 3.0 vol %.

The structure of the discharges in the gas phase between the dielectric and the polymer solution with BaTiO₃ nanoparticles was recorded by an electron-optical transducer (Fig. 26). As is seen, the discharge forms at various sites of the dielectric surface and the polymer solution.

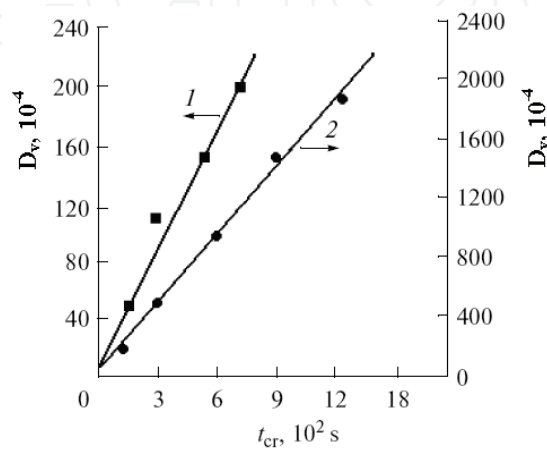


Fig. 25. Change in the optical density of the bands evolved in the IR spectrum of the polymer phase of the composite PVDF+50 vol % PZT-5A during the electrothermodischarges of the crystallization. The cooling rate is 2K/min. $U_p = 11.8 \text{ kV}$, $W = 1.4 \times 10^{-6} \text{ J}$. (1) $\nu = 3380(\text{OH})\text{cm}^{-1}$, (2) $\nu = 1735(\text{C-O}) \text{ cm}^{-1}$ and (3) $\nu = 1280(\text{C-O-C})\text{cm}^{-1}$.

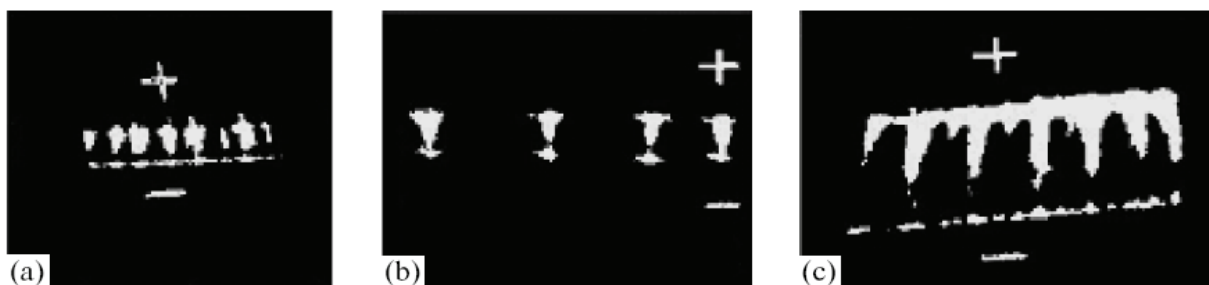


Fig. 26. Optical image of the development of microdischarges in the air medium between the dielectric (polytetrafluoroethylene with a thickness $d = 2 \text{ mm}$) and the surface of the polymer solution. (a) $d = 4 \text{ mm}$, (b) $d = 6 \text{ mm}$, and (c) $d = 10 \text{ mm}$; $U = 35 \times 10^3 \text{ V}$.

Let us consider the technology of the preparation of the hybrid composed of nano- and micropiezoelectric composites. We used for the first time the effect of nanostructuring of polymers for the creation of a novel class of piezoelectric composites. A general model and a scheme of the individual steps of the technology suggested are given in Fig. 27. The technology involves the following main stages: the preparation of the piezo-composite composed of micropiezoceramic particles, a polymer interface layer, and a near-surface polymer region (Fig. 27, a); the dissolution of the near-surface polymer phase (area) and the preparation of the piezo-composite structure (substrate) composed of piezoceramic particles

and the polymer interface layer having direct contact with the piezoparticles (Fig. 27, b); the nanostructuring of the dissolved polymer phase (Fig. 27, a, element 3) by the dielectric BaTiO_3 nano-particles; the chemical precipitation of the nanostructured dissolved polymer on the surface of the piezo-composite substrate; and the preparation of the hybrid (Fig. 27, c) from the polymer–nanoparticles BaTiO_3 and polymer–micropiezoceramic particle matrix systems.

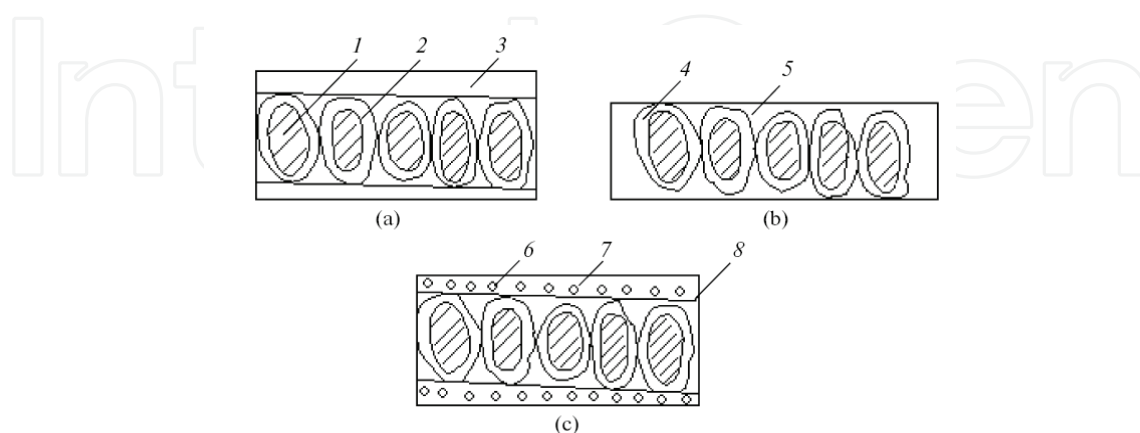


Fig. 27. Scheme of the structure formation of the hybrid of nano- and micropiezoelectric composites PVDF – nanoparticles and BaTiO_3 – piezoceramics PZT-5A. (a) micropiezoelectric composite PVDF – PZT-5A, (b) the micropiezoelectric composite in the case of the dissolved subsurface polymer layer, and (c) the hybrid nano- and micropiezocomposite PVDF – BaTiO_3 – PZT-5A: (1) piezoparticles, (2) interface polymer layer, (3) subsurface polymer range (phase), (4) interface layer in the case of the absence of the subsurface polymer range, (5) piezo-composite structure (substrate) (b. 5), (6) nanoparticles BaTiO_3 , (7) nanostructure polymer subsurface layer, and (8) nano- and piezohybrid composite.

5. Conclusion

So, the wide investigations were carried out in range of physics and technology of active dielectrics – from synthesis of new polymers, ferropiezoelectrics, semiconductors, nano- and microcomposites till creation of hybrid composites, in particulars, hybrids on the basis of matrix nano- and micropiezoelectrics. For creation functional ensembles including micro- and nanopiezoelectric composites (synergetic system) we need to know how these structures can joint each with other, to know possible methods of nano- and micro composites interconnection into ensembles.

It is possible to synthesis nanoscale particles with regulated sizes and compounds, and then to immobilize these particles in polymer phase possessing unique properties. In chapter of this book this problem was solved by next way: 1) Firstly, the experimental results on determination of the role of interface electron-ion and polarized processes for formation of piezo- and pyroelectric properties of composites are considered. 2) The role of electronic properties of interface boundaries are revealed; it is shown that a formation of quasi neutral system on the interface, injected charge in process of polarization and an oriented domain are key factors for formation of high piezo-, pyroelectric and electret properties. 3) Local energetic levels of high concentration and activation energy are created by crystallizing of polymer under the conditions of plasma of electric discharge; the presence of such deep

traps on the interface increases essentially electrophysical properties of composites owing to increasing value of re-orientation polarization of piezophase. 4) It is revealed that intensive oxidation of polymer phase under the action of plasma of electric discharge reduces essentially a mobility of macromolecules on the interface owing to growing interface interactions and promotes increasing of electromechanical properties of composites. 5) By investigation of influence of piezoelectric particles sizes on electromechanical, mechanical and electrophysical properties it is determined that decreasing of particle sizes is accompanied by increasing of mechanical characteristics of composites and decreasing of piezo-, pyro- and electret properties. 6) By investigation of physical-mechanical properties of composites, using nanosized CO₂ and BaTiO₃ particles as inorganic phase, it is determined that the nanodispersion of polymer phase leads to noticeable increasing of mechanical and electromechanical parameters of composites. 7) The noticeable difference of molecular moving and supramolecular structures of polymer matrix on the interface and in the volume, where the influence of piezoelectric particles is absent, promoted a development of hybrid active composites based on the matrix nano- and micropiezoelectric composites.

6. Acknowledgment

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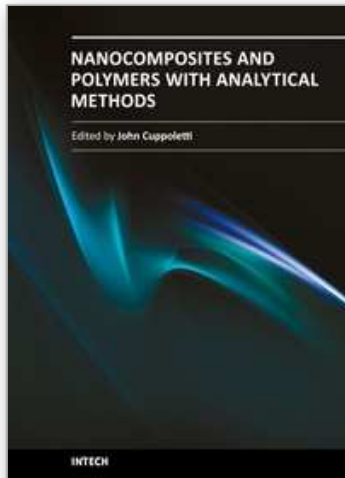
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