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# New materials for the electromechanical and acoustoelectric transducers

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## ABSTRACT

The technology for creation of the polymer-microsized piezoelectric composite substrate is developed by employing the electric gas discharge plasma method. It is determined experimentally that as a result of the nano-structurization of the volume of the polymer-piezoceramic composite close to the surface it is Young and piezomodulus as well as the mechanical quality and electromechanical coupling coefficients and the dielectric constant has been increased, whereas, tangent losses are decreased depending on the type of the nanoparticle and its volume rate.

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Nanoarticles; piezoelectric substrate; polymer-piezoceramic composite

## 1. Introduction

The development of the immobilization technology of the nanoparticles in the various polymer-based composites is one of the open problems of nanotechnologies and nanomaterials science [1,2]. This problem can be solved by applying electrical gas-discharge plasma that appears as a result of the action of the high voltage in the gas region surrounded by dielectric materials [3]. Nanosized particles have sufficiently high activity and wide surfaces, same time they are sensitive to impurities, active centers, and functional groups [4]. In solution, these particles can form a compound with each other very quickly and then the mobilization effect becomes stronger as a result of an increase in their concentration.

Piezoelectric transducers operate both as receivers of the acoustic waves and their generators [5,6]. Despite that the performance of the piezoelectric composites as receivers of the acoustic waves (e.g. microphone regime) is twice higher being compared with the performance of the similar piezoceramic elements, however, the power of the generated signals in the regime of the acoustic waves is weak due to that, their electromechanical properties are sufficiently small. The reason for the low efficiency of the piezoelectric composites in the acoustic waves generator regime is the small value of their mechanical voltage and Yung's modulus, but also their significant mechanical loss. One can conclude that the small values of the listed above electromechanical parameters ( $Q_m$ ,  $Y_{II}^E$ , and  $S_{II}^E$ ) of the composite and its higher  $\tan\delta$  mainly is related to the chemical structure of the polymer matrix of the composite material itself [7]. It is known that

absorption of the acoustic waves' energy results in its transformation to nonrenewable energy, i.e. heat. The main reason for the appearance of this effect is the difference in the phases between the periodic change of the medium density and the pressure of the sound waves. Such an effect exhibits itself more in systems which have high heterogeneity similar to composite materials because composite materials are compounds consisting of a number of components with different acoustic resistances. Due to the appearance of the difference in the acoustic resistance of the components reflectance effect also becomes important along with absorptance and scattering effects. Regardless of the technology of obtaining piezoelectric elements, electrets, and pyroelectric composites, the formation of the rich phase always exhibits itself on the surface of these composites. In this case, efficiency and electromechanical coupling factors of receiving or generation of the acoustic waves regime of the listed above active domains become low, whereas their mechanical and electrical losses increase. Therefore, the closeness of the values of the acoustic resistance of the components especially for piezoelectric elements is a mandatory condition. In order to achieve this condition, one can employ here recent advances in nanotechnologies – to replace the volume of the polymers located close to the surface of the active composites with the nanostructured polymer composites [8].

## 2. Methodology

We use the polymers mainly consisting of polyolefine and fluorine as a piezoelectric composite substrate. Polyvinylidene fluoride (PVDF) is one such material [9]. PVDF acquires its piezoelectric property only after electrothermal polarization and special mechanical treatment. Its piezoelectric coefficient  $d_{ij}$  being different from the inorganic piezoelectric materials is defined not as a result of displacement of the ions in the crystalline lattice, but through the supramolecular structure. The physical structure of polymers with the piezoelectric properties consists of crystallites with certain dipole moments and amorphous phases behaving themselves like matrices. During the electrothermal polarization process, both volume charges appear and a local electric field is formed on the border of the amorphous phase and quasicrystals. Then, under the joint action of the local electric field and temperature, the quasicrystals having the dipole moment become oriented in the direction of the electric field. If one cools the polymer element without interruption of the action of the electric field, then the reorientation polarization will be formed. It is known that the piezoelectric coefficient is defined through the reorientation polarization  $P_r$ , that is,

$$d_{ij} = P_r \cdot \varepsilon_{ij}. \quad (1)$$

This means that the stability of the action of the  $d_{ij}$  coefficient to the electric, temperature, and mechanical fields is defined by the stability of  $P_r$  and  $\varepsilon_{ij}$  parameters with respect to the listed above factors.

Nanoparticles, such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{BaTiO}_3$  are the main components of the nano-polymer composites [10,11]. One needs to note that using the ferroic materials belonging to the multicomponent  $\text{Pb}(\text{ZrTi})\text{O}_3$  family for the creation of the nano-piezoelectric materials is of particular importance. However, the thorough information in the scientific literature about obtaining the nano-sized particles from the multicomponent

piezoceramics belonging to  $\text{Pb}(\text{ZrTi})\text{O}_3$  family is simply lacking. Micro-sized particles of the ceramics of the  $\text{Pb}(\text{ZrTi})\text{O}_3$  origin have a stable structure and at present, they have successful applications as matrix-type polymer composites for wide-range use. We suppose the matrix-type polymer materials, which consist of the hybrid of the polymer composites formed from the nano- and micro-sized piezo-particles. A nanostructured layer close to the surface is chemically deposited into the piezoelectric substrate. Thus, the polymer layer deposited into the piezoelectric substrate becomes nanostructured in the hybrid-type composite and it replaces the layer close to the surface in the matrix-type composite. This phase deposited into the piezoelectric substrate will have very high physical and mechanical properties. In the composites having hybrid structures, the polymer-piezoceramic substrate defines the micro-piezoelectric phase, whereas polymer- $\text{BaTiO}_3$  or polymer- $\text{SiO}_2$  defines nanophase.

### 3. Experimental

The creation of the piezo-substrate dispersed with the micro-sized PZT type piezoelectric particles is the main problem of the development of technology of hybrid piezoelectric materials [12]. Because the piezo-substrate defines the piezoelectric properties of the hybrid composites. Thus, the solution to this problem requires the thorough study of the surface of the microstructured composites by more efficient methods taking into account their physical and chemical structure. The application of the barrier-type electric gas discharge plasma as a wearing factor on the surface of the electronics element plays an important role in nanotechnologies. Development of new technologies and constructions, which will provide the stability of the parameters of the main element of the hybrid composites – piezo-substrate under the joint action of the external factors is required.

Electric gas discharge plasma in the airspace surrounded by the dielectric is used for wearing or erosion under the influence of the various external factors of the surface of the piezoelectric element. This technology consists of two stages:

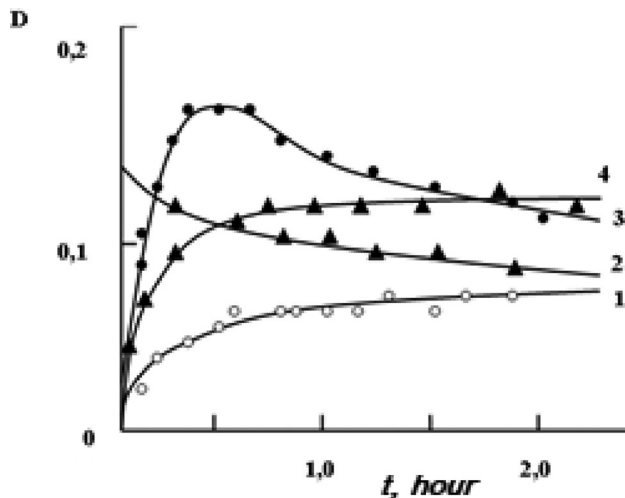
- Erosion of the surface of the piezoelectric element by the use of electric gas discharge in the airspace surrounded by the dielectric being appeared as a result of the action of high voltage;
- Cleaning of the surface of the piezoelectric element being subjected to strong erosion, under the joint action condition of the Toluene solution and temperature.

The goal can be achieved via the following two approaches:

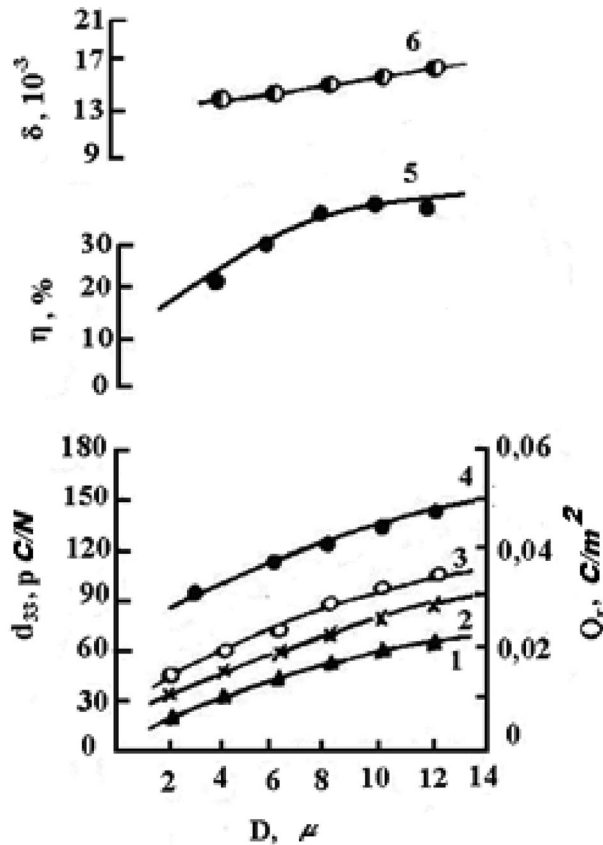
- To dissolve the volume of the piezoelectric element close to its surface as much as possible by using various solvents, especially those having a higher boiling temperature (toluene, benzene, and xylene) – in this case, the structure of the interphase border that element forms together with polymer microparticles, should stay stable;

- Wearing or erosion of the surface of the piezoelectric element under the influence of the various external factors.

Both methods are based on the statement that the melting temperature of the polymer part of the piezoelectric element close to the surface is sufficiently less than the melting temperature of the polymer that is formed in the interphase border under the influence of the piezo-particle. Performed experiments show that the first approach is completely appropriate to achieve the main goal. However, this approach requests a longer time. Taking this into account, the present experiment follows the second approach, that is, wearing of the polymer layer. In order to achieve the aim, electric gas discharge plasma in the airspace surrounded by the dielectric has been used. One can say that the wearing of the piezo-substrate surface is defined in general via the energy in the contact area of the substrate submitted by the plasma channel. As a result of the influence of this energy, the surface of the piezo-substrate warms leading to a favorable environment for the thermo-oxidation reaction and further erosion of this surface. The role of the oxygen origin small molecular groups synthesized in the plasma channels in the formation of the processes under the influence of the barrier type electric gas discharge is very high. In Fig. 1, the dependence of such groups appeared under the condition of the electric gas discharge at PVDF from the wearing time is presented. One observes here that this dependence obeys quite complex law. However, the  $D = f(t)$  dependence belonging to the  $\text{CH}_2$  group is constant. The main reason that the dependence of the volume of shown groups from the wearing time is constant, can be explained by the completion of the erosion process after the modified time. We employ a change of optical density of the  $\text{CH}_2$  group for the prognosis of the erosion processes in the polymer matrix being used. The character of the change of optical density of the  $\text{C}=\text{O}$ ;  $\text{OH}$ ;  $\text{CH}_2$  groups allows for prognosis of the processes that appear in the



**Figure 1.** Dependence of the optical density of bands in the IR spectrum of the PVDF from the wearing time. (1)  $3200\text{ cm}^{-1}$  –  $\text{OH}$ ; (2)  $4327\text{ cm}^{-1}$  –  $\text{CH}_2$ ; (3)  $1700\text{ cm}^{-1}$  –  $\text{C}=\text{O}$ ; (4)  $1278\text{ cm}^{-1}$  –  $\text{C}-\text{O}-\text{C}$  groups. The thickness of the airspace surrounded by the dielectric created by the electric gas discharge is  $d = 4\text{ mm}$ , and the voltage applied to the plasma is  $U = 20\text{ kV}$ .



**Figure 2.** Dependence of the composite parameters  $d_{33}$ ,  $Q_r$ ,  $\eta$ , and  $\delta$  from the size  $D$  of the piezoceramics domains. The curves 1 and 3 belong to composite PP-PKR-8 and the curves 2 and 4 belong to composite PP-PKR-3. Polarization conditions:  $E_p = 4.5$  MV/m,  $T_p = 393$  K and  $t_p = 0.5$  h.

piezoelectric substrate under the influence of the barrier type electric gas discharge as well as makes it possible to preserve the piezoelectric substrate against any mechanical damages.

Our previous experimental results allow us to select a suitable piezoceramic phase of the composite piezoelectric substrate [13–15]. We determined from the experiments that the piezoelectric substrate being a main phase of the hybrid composites should have the following properties:

1. The structure of the piezoceramic phase of the composite piezoelectric substrate should be rhombohedral ( $R_e$ ) or heterogeneous ( $R_e + T$ ).
2. Reorientation polarization being formed during the polarization process should be high and stable.
3. The orientation degree of the domains different than the  $180^\circ$  domain of the piezoelectric phase ( $71^\circ$ ,  $90^\circ$ , and  $109^\circ$ ) should be high.
4. The diameter of the domains of the piezoelectric phase should be as big as possible (Fig. 2).

5. A sharp increase in the amount of stabled electrical charge ( $Q_r$ ) and piezoelectric module ( $d_{33}$ ) in the interphase border of the composite should happen in case of the increased diameter of the domains.
6. Spontaneous deformation ( $\eta$ ) of the perovskite core of the piezoelectric phase should be increased in case of the increased diameter of the domains.
7. Interactions should be high in the interphase border of the composite piezoelectric substrate.
8. Polymer matrix in the composite piezoelectric substrate should be polar.
9. The activation energy of the stabled electrical charge carriers should be higher than the activation energy of the piezoelectric phase domains of the substrate during the polarization process in the interphase border of the composite piezoelectric substrate.

Based on a number of the experimental results, it is known that  $d_{33}$ ,  $\epsilon_{33}$ , and  $g_{33}$  parameters in the 3 – 0 structured composites vary in dependence from the Lead Zirconate Titanate volume proportion as follows:  $d_{33}$  and  $\epsilon_{33}$  increase monotonously, whereas,  $g_{33}$  at first increases, achieves its maximum and then decreases. It is proven that regularities of change of these parameters in dependence on the volume proportion of the piezoelectric phase, in general, depend on the concentration and activation energy of the electrical charge carriers stabled in the interphase border. One needs to note that the importance of the electrical charge carriers formed in the interphase border of the composites as a result of the electrothermal polarization for 3 – 0 structured composites is higher than for 3 – 3 and 3 – 1 structured ones. One can control  $d_{33}$ ,  $\epsilon_{33}$ , and  $g_{33}$  parameters in the wide interval by changing systematically the volume proportion of phases, electrical charge state, and electrophysical properties in the composite. Then, one observes that nano-structurization of the polymer matrix leads to the increase of the concentration and activation energy of the electrical charge state of the interphase border and border stabilization centers. It is known that the successful application of hybrid piezoelectric materials as acoustic receiving and transmitting antennas, piezo-transformer, filters, and piezo-engines requires that these materials should have a special higher force. The following statements should be valid for such piezoelectric materials in order to achieve this requirement:

- Constant behavior of the self-mechanical quality coefficient  $Q_m$  during the action of the exciting high electric field;
- High behavior of the operating temperature range;
- Stability of  $K_{ij}Q_m$  indicator under the action of the high static and dynamic mechanical voltages.

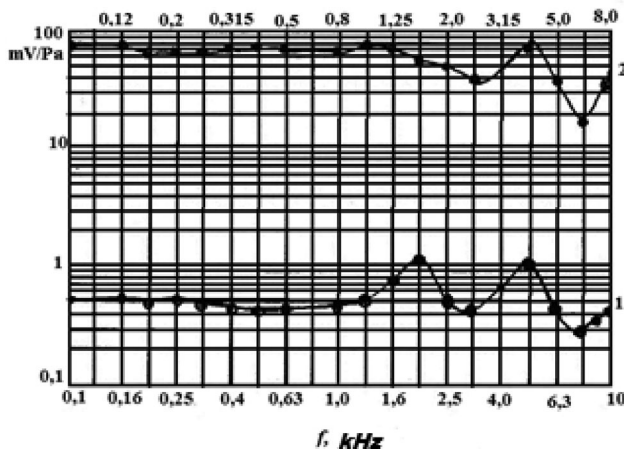
We achieved these requirements by solving the problem as follows:

1. Crystallization of the composites with the various structure piezo-phase ( $PbTiO_3$ -  $PbZrO_3$ -  $PbNb_{2/3}Mn_{1/3}O_3$ -  $PbW_{1/2}Mg_{1/2}$ ) and polymer matrix under the action of the electrical gas discharge;

2. Creation of the piezoelectric materials based on the hybrid of the composites having the nano- and micro-sized piezo-phase with the polymer matrix.

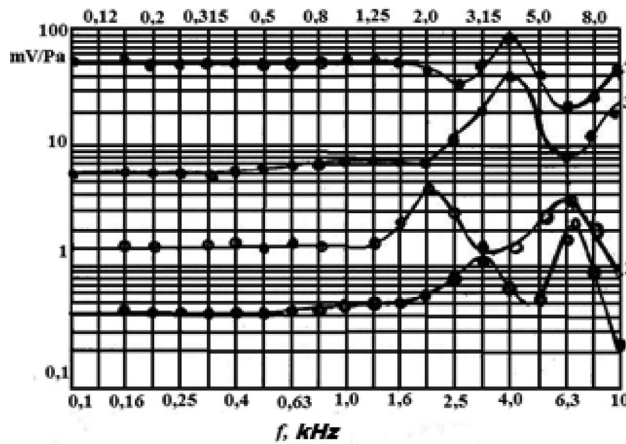
In Fig. 2, the change of the  $Q_m$ ,  $K_{31}^2 Q_m$ ,  $\eta$ , and  $\delta$  parameters of the composites created under the gas discharge process on the base of the structure and  $PbTiO_3$  component concentration of the piezo-phase is depicted. One can observe from this figure that the  $Q_m$  parameter of the piezo-phase in the compounds with the rhombohedral structures is higher than in compounds with the tetragonal structures.  $Q_m$  parameter achieves its minimal value at hybrid ( $T + R_e$ ) structured piezoceramics. At the same time,  $K_{31}^2 Q_m$  parameter achieves its maximal value at the rhombohedral phase. Above, the correlation is studied between  $Q_m$  and  $\eta$  and  $\delta$  structure parameters.  $\eta$  and  $\delta$  are characteristics of the domain structures:  $\delta$  is related to rapidity, whereas,  $\eta$  is a parameter connected with a number of the domain borders. These factors define the change of  $Q_m$ . When the amplitude of the dynamical voltage ( $\sigma$ ) increases, then the parameter  $Q_m^\sigma$  (mechanical quality factor) decreases (Fig. 2, curve 4). Dependence of the mechanical quality from the content (concentration of  $PbTiO_3$ ) in the morphotropic region (small exciting regime –  $Q_m$ ) achieves its minimal value, however, for all structures the condition  $Q_m > Q_m^\sigma$  holds. The main reason for this effect is an increase in the rapidity of domain borders at high amplitudes of the mechanical voltage (dynamical regime). In its turn, it results in decrease of the mechanical quality ( $Q_m < Q_m^\sigma$ ).

One of the important factors, that is necessary to take into account is the transformation of the space of the nanoparticles' location to the stabilization centers for the electrical charge carriers injected under the electrothermal polarization process. These spaces are equivalent to the production of the local levels at the quasi-bandgap of the polymer matrix. As we noted before, an increase in the piezoelectric, mechanical, and electromechanical effects exhibits itself in both generations and receiving of the acoustical waves (Fig. 3).



**Figure 3.** Dependence of the sensitivity ( $mV/Pa$ ) of the acoustoelectric transducer created on the base of the hybrid piezoelectric materials from the frequency. (1) PVDF – 50% PKR – 3M microcomposite. (2) PVDF – 1.5% volume, nanosize  $BaTiO_3$  – 48.5% PKR – 3M hybrid composite; polarization conditions:  $E_p = 4.5$  MV/m,  $T_p = 393$  K,  $t_p = 0,5$  h.





**Figure 4.** Dependence of the sensitivity ( $mV/Pa$ ) of the acoustoelectric transducer created on the base of the hybrid piezoelectric materials from the frequency. (1) The composite based on the ASPE and microsized piezophase (PKR-8); (2) ASPE – 1.5% volume, nanosize  $BaTiO_3$  phased – 48.5% PKR – 8 hybrid composite; (3) PP – 50% PKR – 8 microcomposite; (4) PP – 1.5% volume, nanosize  $BaTiO_3$  phased – 48.5% PKR – 8. Polarization conditions:  $E_p = 4.5$  MV/m,  $T_p = 393$  K,  $t_p = 0.5$  h.

By comparing the amplitudes and frequency ranges of the transducers prepared on the base of the various composite piezoelectric materials, one can deduce that hybrid composites are more effective transducers (Figs. 3 and 4): their frequency range is wide, the signal amplitude is high, the approximate stable part of their Voltage-Current characteristics is shifted to the high-frequency region, and the nonlinearity of their amplitude-frequency characteristics is reduced. Curve 2 of Fig. 3 corresponds to the frequency characteristics of the sensitivity of the hybrid composite  $PVDF - 1.5\% BaTiO_3 - 48.5\% PKR-3M$  in its operation as the receiver regime of the acoustic waves. Here, curve 1 corresponds to the analogical characteristics for  $PVDF - 50\% PKR-3M$  micro-composite. One easily observes from these dependencies that the sensitivity ( $mV/Pa$ ) of only the linear-like part is different  $10^2$  times.

In Fig. 4, the amplitude-frequency characteristics of the hybrid composites based on matrices ASPE, PP, and PVDF are presented in order to determine the influence of the composite piezo-substrates on the acoustic transducers of various functions created on these substrates. It becomes clear from the comparison results of Figs. 3 and 4 that both amplitudes and frequency ranges of acoustoelectric transducers substantially differ from each other depending on the content of piezo-composite substrates. In the initial approach, PVDF, and already modified under the action of the plasma of the electric gas discharge PP are more effective. However, one needs to note that the complete selection of the content of hybrid piezoelectric materials, their modification, and polarization regimes are not completely optimized in the current work. The solution to this problem requires a lot of experiments, which have to study thoroughly the influence of the content of hybrid composites, the structure of the components, their modification conditions, and interphase interactions on the macroscopic characteristics of the created final version of the acoustoelectric and electroacoustics transducers.

## 4. Conclusion

1. The technology of creation of the polymer - microsized piezoelectric composite substrate is developed by employing the electric gas discharge plasma method;
2. It is determined experimentally that as a result of the nano-structurization of the volume of the polymer-piezoceramic composite close to the surface its Young modulus has been increased 5.4 times, piezo-modulus has been increased twice, the mechanical quality coefficient has been increased 6 times, the dielectric constant has been increased twice, electromechanical coupling coefficient has been increased 1.6 times, whereas, tangent losses are decreased 3–6.5 times depending on the nanoparticle type ( $\text{SiO}_2$  and  $\text{BaTiO}_3$ ), and its volume rate;
3. Frequency range of the outgoing signal of the piezoelectric materials created as a hybrid of the polymer-nano- and polymer-microphase composites is significantly higher than the similar indicator of the polymer-microphase composite.

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