

Composite materials ferroelectric ceramics–polymer for hydroacoustic receivers*

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The purpose of this work is to study the processes of interfacial interactions, their influence on the piezoelectric properties in highly elastic composite structures, to establish the patterns that determine the volume-sensitive piezoelectric characteristics of composites and to create effective piezoelectric materials for hydroacoustic receiving devices. In the process of this work, the development of a method for obtaining anisotropic ferroelectric ceramics, the development of methods for the preparation of perfect ceramic powders and composite materials based on thermoplastic fluoropolymers and the study of composite materials based on lead–calcium titanate were carried out. As a result of the study, the dependences of the hydrostatic parameters of the composites on the degree of filling, particle size distribution, piezoelectric anisotropy of the active phase and the elastic properties of the polymer matrix were established. Composite materials were based on ceramics of the PT–CT system and thermoplastic fluoropolymers F-2ME, F-62, F-2N with a degree of filling with a ceramic phase from 30 to 60% vol. The dependences of the hydrostatic piezoelectric moduli g_h and d_h , and the quality factor $g_h d_h$ on the degree of filling of the composite for polymers F-62 and F-2ME with different average sizes of ceramic particles are plotted. It has been established that the maximum values $g_h = 119.1 \cdot 10^{-3}$ V·m/N and the quality factor $g_h d_h = 6074 \cdot 10^{-15}$ m²/N are achieved for a polymer with a higher elastic compliance (F-62) at a degree of filling of 60% vol. and the use of granular filler.

Keywords: Piezomodule; ferroelectric ceramics; lead titanate; calcium titanate; composite ceramics–polymer.

1. Introduction

Modern research in fundamental materials science is aimed at the problems of establishing general crystal-chemical patterns of formation of substances; stability of their structures; processes of restructuring and self-organization of structures, including mechanisms and patterns of formation of structures at the mesolevel in the areas of the boundaries of sections and conditions for the organization of continuous and quasi-continuous structures at micro, meso and macrolevels; relationships, interactions and mutual influence elastic and electrical subsystems. Currently, all these studies, and, in particular, studies of electrical and elastic subsystems, electromechanical and mechanoelectric interactions and effects, have focused on heterogeneous materials, which is due, on the one hand, to the fact that heterogeneous systems are of exceptional interest for conducting a very wide range of fundamental research on the above problems, and, on the other hand, practically important applications of these materials.

Currently, ferroelectric ceramics acts as the main active material of converters and devices using the piezoelectric effect. The main types of piezoceramic materials and the technological methods of their preparation as a whole have already been formed, and the functional parameters cannot be further significantly improved by selecting the optimal chemical composition, synthesis conditions, sintering, testing of

polarization modes, etc. In particular, piezoelectric ceramics based on solid solutions of zirconate-lead titanate (PZT) and barium titanate (BT), as well as piezoelectric polymers such as polyvinylidene fluoride (PVDF) and its copolymer with trifluoroethylene (P(VDF-TrFE)) are widely used as hydroacoustic receiving materials. At the same time, these materials have a number of disadvantages in terms of their use in hydroacoustics. First, although the absolute magnitude of the piezoelectric modules d_{33} and d_{31} of PZT and BT is large (100–600 pC/N), the hydrostatic piezoelectric module $d_h = d_{33} + d_{31} + d_{32}$ is relatively small due to the fact that $-(d_{32} + d_{31}) \sim d_{33}$. Second, since these ceramics have a high relative permittivity of $\varepsilon_{33}^T/\varepsilon_0 \sim 1000$ –4000, their hydrostatic piezoelectric modulus $g_h = d_h/(\varepsilon_{33}^T/\varepsilon_0)$ is small. Third, there is a large difference in the magnitude of the acoustic impedance Z between piezoelectric ceramics and the sound wave propagation medium, as a result of which the use of matching layers is necessary to suppress the effect of reflection of the sound wave at the interface. Fourth, when using piezoelectric ceramics in hydrophones, complex and expensive mechanical designs of transducers (for example, a cylindrical configuration with end caps) are usually used to increase sensitivity, allowing to suppress the transverse direction of polarization of the component of the sound pressure wave, or convert it into a longitudinal one. Fifth, ceramics are brittle, have low resistance to shock loads,

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bending and are difficult to process. Sixth, due to the high mechanical Q -factor Q_m , the use of additional damping layers is necessary to increase the attenuation of vibrations. Piezoelectric polymer materials are plastic, have an acoustic impedance close to water and a large g_h value. However, a low value of the relative permittivity of the polymer ($\epsilon_{33}^T/\epsilon_0 < 15$) leads to a loss of receiver sensitivity when the piezoelectric element is paired with a voltage amplifier. Additionally, because of the high electric fields required for polymer polarization, it is difficult to polarize samples with a thickness of more than 0.5 mm.

Thus, traditional piezoceramic materials have a number of limitations when used both in ultrasonic flaw detection and medical diagnostics, and in hydroacoustics. In this regard, the development of composite piezoelectric materials composed of two or more phases, at least one of which is piezoactive, has been actively developed. The basic principles of constructing electrically active composite ceramic materials, including the classification of their physical properties, the description of symmetry and its effect on properties, the concept of connectivity of the phases composing the composite material, were developed in the 1980s, mainly in the Materials Research Laboratory of Pennsylvania State University (USA) and are described in detail in several review papers.¹⁻⁴ Of the greatest practical importance are piezoelectric composite materials ceramics–polymer with connectivity type 1–3 (2–2), mixed composite materials ceramics–polymer with connectivity type 0–3 and porous ceramics, which, depending on open or closed porosity, can be considered as a composite material ceramics–air with connectivity type 3–3 and 3–0, respectively. All of these materials have a lower density and acoustic impedance compared to ceramics, as well as a lower mechanical Q -factor. In addition, they are characterized by a decrease in the Poisson's ratio, which binds the elastic constants of the material in the longitudinal and transverse polarization directions. Therefore, the contribution of the piezoelectric modules d_{31} and d_{32} to the hydrostatic receiving sensitivity of the material is suppressed⁵ and the relationship between the vibration thickness mode used in the detection and diagnostics of defects and parasitic radial vibrations is reduced. Due to the relative simplicity and cheapness of production, the main practical value of ceramic–polymer composite materials with a type of connectivity 0–3, which are piezoelectric ceramic powder evenly distributed in a polymer matrix, lies in the possibility of manufacturing homogeneous large-sized plates of matrix converters, coaxial cores of extended acoustic cable antennas and cylindrical converters used in hydroacoustic receivers.⁶ As a rule, they are designed for long-range detection systems of underwater objects operating in the frequency range up to 1 kHz.

The analysis of the literature data indicates that theoretical and experimental studies of composite materials piezoelectric ceramics–polymer in general and, with the type of connectivity 0–3 in particular, are at an initial. At the same time, there has been a practical interest in specific hydroacoustic

receiving devices based on composite materials of this type. Therefore, topical tasks are to study the processes of interfacial interactions in highly elastic composite structures and to establish patterns that determine the volume-sensitive characteristics of composites and directed modeling and creation of effective piezoelectric materials for hydroacoustic receiving devices

Composite materials “piezoelectric ceramics–polymer” with connectivity type 0–3, which are ceramic powders evenly distributed in a polymer matrix, are the most mass-produced and inexpensive type of piezoelectric composites designed for hydroacoustic receiving devices. For this field of application, it is necessary that the composite material has the maximum value of the product of hydrostatic piezoelectric modules $g_h \cdot d_h$. Therefore, as a rule, solid solutions based on PbTiO_3 with high anisotropy of piezoelectric modules $|d_{33}/d_{31}| \gg 1$ and $d_h \approx d_{33}$, $g_h \approx g_{33}$ are used as the ceramic phase. The choice of a polymer matrix is determined by the need to coordinate the dielectric permittivity of the polymer and ceramics in order to ensure effective polarization of the composite material. For practical use, it is also necessary that the polymer filled with ceramics can be processed by extrusion. A detailed analysis of the current state of research in this area was given by the authors earlier.¹

This paper presents the technology of the preparation of piezoelectric composite based on ceramics $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.05}\text{Ti}_{0.95}\text{O}_3$ and thermoplastic fluoropolymers F-2ME and F-62, which are PVDF copolymers, produced by JSC “Plastpolymer”, St. Petersburg.² Ceramics $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.05}\text{Ti}_{0.95}\text{O}_3$ has a relatively low permittivity value $\epsilon_{33}^T/\epsilon_0 = 200$ and small dielectric losses $\text{tg}\delta = 0.015$. The value of the longitudinal piezomodule $d_{33} = 68$ pC/N, the transverse piezomodule d_{31} is zero. Fluoropolymers F-2ME and F-62 have similar dielectric properties: Relatively high permittivity values ($\epsilon_r = 9$ –10) and low dielectric losses ($\text{tg}\delta = 0.012$ –0.020), high electrical strength (21–25 kV/mm); however, they differ significantly in elastic and strength characteristics (Table 1). F-2ME is a harder and tougher material.

2. Experimental Methods

The starting material of the composition $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.05}\text{Ti}_{0.95}\text{O}_3$ with the addition of 1% by weight. MnO was obtained by two-stage solid phase synthesis according to the method described in Ref. 3.

The previously studied materials with different calcium content were selected as the object of the study: $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.05}\text{Ti}_{0.95}\text{O}_3$ (I), $\text{Pb}_{0.70}\text{Ca}_{0.30}(\text{Co}_{0.5}\text{W}_{0.5})_{0.05}\text{Ti}_{0.95}\text{O}_3$ (II) and $\text{Pb}_{0.66}\text{Ca}_{0.34}(\text{Co}_{0.5}\text{W}_{0.5})_{0.06}\text{Ti}_{0.94}\text{O}_3$ (III) with the addition of 1 wt.% MnO.¹ PbO, CaCO_3 , TiO_2 with the content of the main substance not less than 99.95% were the initial reagents.

Since the main difficulties in the synthesis of the material were reduced to the introduction of calcium oxide into the

Table 1. Main technical characteristics of thermoplastic fluoropolymers.²

Properties	F-2ME	F-62
Density, kg/m ³	1780	1790
Tensile strength, MPa	45–55	20–36
Elongation at break, %	450–550	630–700
Brinell hardness, MPa	90	30
Destructive stress during static bending, MPa	54–83	27
Modulus of elasticity at static bending, MPa, at 20°C	930–1400	200–275
Melting point, °C	148–150	110–130
Decomposition temperature, °C	350	360
Operating temperature range, °C	–40 ÷ 135	–60 ÷ 120
Specific volumetric electrical resistance, not less than, Ohms·m	5·10 ¹⁰	4·10 ¹²
The tangent of the dielectric loss angle at 10 ³ Hz	0,012–0,02	0,02
Electrical strength, kV/mm	25	21
Dielectric constant at 10 ³ Hz	9–10	9

vehicle, we developed a synthesis scheme using an intermediate compound—calcium titanate CaTiO₃ (CT). Our research has shown that the qualification of the titanium dioxide used has the greatest impact on the manufacturability and quality of the material.

The corresponding oxides and CT were loaded into a polyethylene drum with jasper balls. The mixing was carried out in aqueous medium for 48 h. The optimal synthesis mode is two-stage: 800°C, 10 h + 900°C from 2 to 4 h with intermediate grinding (24 h). The completeness of the synthesis was controlled by X-ray phase analysis, it was at least 95%. The presence of free calcium oxide was controlled by the pH of the grinding medium.

The material was sintered in air at 1080–1110°C (ceramic I), 1130°C (II) and 1150°C (III). The exposure time was 4–5 h. The density of the resulting ceramics is at least 95% of the theoretical one.

Optical examination of the powders was carried out on a Neofot-21 microscope using a transmitted light prefix. The powders were placed on a slide and their dispersion was evaluated directly on the device.

Electrophysical studies to determine the piezoelectric parameters of the ceramic material were carried out on samples in the form of disks with a diameter of 9 mm and a thickness of 0.5 mm with embedded silver electrodes. The polarization of ceramics I was carried out at room temperature, the polarization time was increased to 0.5 h for complete redistribution of the internal displacement field. The selected value of $E_p = 60$ kV/cm is optimal for obtaining the minimum value of the K_p and, at the same time, does not lead

to microcracking, which reduces the likelihood of electrical breakdown. Similarly, Ceramics II and III were polarized.

X-ray diffraction analysis of powders was performed on a DRON-3 diffractometer with Bragg–Brentano focusing on Fe K_α radiation (Mn-filter). The sizes of the coherent scattering regions D and the microdeformation values of microdeformations $\Delta d/d$ were determined by the analytical approximation method using Cauchy functions.⁴

3. Results and Discussion

The properties of the samples of all three ceramics are shown in Table 2.

It can be seen that the piezoceramic I is the most promising for use in ultrasonic transducers of nondestructive testing devices and medical diagnostics. This is primarily due to the magnitude of piezoanisotropy ($K_t/K_p \sim \infty$) at $K_t > 0.5$, low values of dielectric permittivity ($\epsilon_{33}^T/\epsilon_0 \sim 200$) and the mechanical Q -factor of the thickness mode of vibrations ($Q_m < 100$). In addition, attention is drawn to the large value of the piezoelectric effect $h_{33} \sim 6.0$ GV/m, which characterizes the sensitivity of the ultrasonic transducer in the receiving mode.

The influence of technological factors on the structural perfection, shape and particle size of powders of anisotropic ferroelectric material of the composition $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.05}\text{Ti}_{0.95}\text{O}_3$ with the addition of 1% by weight is considered. MnO obtained by two-stage solid phase synthesis according to the procedure is described in paragraph 1.

The direct introduction into the polymer of a synthesized powder intended for sintering high-density ceramics does not allow achieving high piezoelectric parameters of the composite material. Methods of additional heat treatment of the synthesized powder are considered and the influence of technological techniques on the degree of perfection of the

Table 2. Material properties of piezoceramics PZT-4.

Parameter	Parameter value		
	I	II	III
ρ , g/cm ³	6.92	6.80	6.67
c/a	1.037	1.027	1.012
$\epsilon_{33}^T/\epsilon_0$	200	315	595
$\text{tg}\delta$	0.040	0.035	0.045
K_p	0	0	0.12
K_t	0.54	0.51	0.45
K/K_p	∞	∞	3.75
Q_m	60	30	20
d_{33} , pC/N	68	67	91
h_{33} , GW/M	6.0	4.9	2.5

obtained particles, their shape, and granulometric composition is investigated.

(1) Since the destruction and subsequent grinding of ceramic blocks is a time-consuming operation and introduces inhomogeneous mechanical stresses into the powder particles, leading to a complication of the domain structure, a technique designed to produce porous ceramics was used for high-temperature firing.² Mixing of the charge consisting of a pre-synthesized piezoelectric material and a poroforming agent was carried out in a polyethylene drum with jasper balls in an isopropyl alcohol medium for 24 h. Ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was used as a pore-forming agent. After drying the resulting mixture at a temperature not exceeding 80°C , it was placed in a closed alundum crucible without briquetting. Heating to 260°C was carried out at a speed of $60^\circ\text{C}/\text{h}$, followed by exposure for 0.5 h, and heating to the sintering temperature at a speed of $200^\circ\text{C}/\text{h}$. The low rate of decomposition of ammonium oxalate contributed to the production of an open porous framework with a uniform pore size. The proposed technique provides more free conditions for the growth of individual grains compared to conventional ceramics and contributes to their enlargement. The resulting highly porous ceramic frame can be easily destroyed mechanically. The ceramic powders were obtained by grinding in a ball mill in an aqueous medium.

(2) The powder prepared by the previous method was treated with a hot 20% HNO_3 solution for 2 h, and then, after washing with distilled water and drying, annealed at 1043°C for 1.5 h. The purpose of chemical treatment is to remove defective and impurity phases located at the boundaries of ceramic grains, giving the grains a rounded shape and dissolving small particles (less than 1 microns) particles. Annealing in the paraelectric phase is designed to eliminate mechanical stresses arising during grinding and simplify the domain structure.

(3) The powder synthesized according to claim 1 was mixed with 5% by weight of 5% aqueous solution of polyvinyl alcohol, formed into briquettes under pressure of 40 MPa and passed through a sieve with a cell size of 1 mm. The granulated powder was poured into an alund box with a layer no higher than 2 cm and fired at 1080°C for 3 h. The resulting sinter was easily destroyed with minor mechanical action. Grinding was carried out in a polyethylene drum dry in the absence of grinding bodies. Using a set of sieves, powder fractions differing in average particle size were isolated.

(4) Earlier,³ we showed that the use of low-melting, easily soluble salts as a transport medium allows increasing the diffusion rate during synthesis, controlling the size and shape of the synthesized powder and increasing the degree of its structural perfection. Therefore, the powder synthesized according to claim 1 was also subjected to heat treatment at 850°C for 3 h in the presence of a KCl melt.

X-ray lines 111 and 222, representing two different orders of reflection from one crystallographic plane, were analyzed. The results obtained are presented in Table 3.

Table 3. Dependence of cell parameters, size of coherent scattering regions and microdeformation of the crystal lattice on the method of preparation of ceramic powder $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.05}\text{Ti}_{0.95}\text{O}_3$.

Methods	a , Å	c , Å	c/a	V , Å ³	D , Å	$\Delta d/d$, $\cdot 10^{-3}$
1	3.896	4.052	1.040	61.52	>1000	1.0
2	3.893	4.059	1.043	61.52	>1000	0.8
3	3.896	4.044	1.038	61.37	720	0.2
4	3.904	4.103	1.051	62.53	1000	1.2

As can be seen from Table 3, the ceramic powder treated with KCl melt differs greatly from the others by the greater magnitude of spontaneous deformation c/a and volume V of the tetragonal perovskite cell. This indicates a violation of the stoichiometric composition of the piezoelectric material due to the diffusion of Ca^{2+} into the melt, which is also indicated by the appearance of weak reflexes characteristic of the structure of rutile TiO_2 on the X-ray.

The powder obtained using granulation has a minimal amount of microdeformations, however, it has a relatively small size of mosaic blocks. Powders obtained by the traditional method and using chemical treatment in combination with low-temperature annealing with large mosaic blocks have large microdeformations.

Since the ceramic powders studied are solid solutions, the chemical heterogeneity of their composition also leads to a physical broadening of the diffraction lines proportional to the value of $\text{tg}\delta$, and this contribution cannot be separated from the contribution of microdeformations caused by inhomogeneous mechanical stresses.⁵ Based on the analysis of the profiles of the remaining X-ray lines on diffractograms, it can be concluded that the effect of chemical heterogeneity of the composition on the physical broadening of the lines is more pronounced for powders obtained by grinding porous ceramics and using KCl melt.

Chemical treatment of ceramic powder and its subsequent annealing can reduce the value of $\Delta d/d$ mainly by removing the defective areas concentrated at the grain boundaries that differ in composition and, to a certain extent, by eliminating inhomogeneous mechanical stresses.

Figure 1 shows the microstructure of studied objects. For the powder obtained by grinding a porous ceramic frame, the particle size ranges from 0.6 to 190 microns, the average size is 5 microns. The shape of the particles of the fragmentation conglomerates has a pronounced cut. In a powder that has undergone chemical treatment and annealing, the particle size dispersion interval is significantly lower than the initial one, from 1.2 to 17.5 microns. The latter is mainly due to the chemical destruction of fragmentation conglomerates and the dissolution of a fine fraction of particles. The average particle size is 4.7 microns. Powders treated with KCl melt differ little from powders that have undergone chemical treatment and annealing, both by the average particle size (4.4 microns) and by the particle size spread interval (1.2–25 microns).



Fig. 1. (a) Powder obtained by grinding a porous framework, $\times 330$, (b) powder obtained by grinding a porous framework with following chemical treatment and annealing, $\times 330$, (c) powder obtained by processing the synthesized material with a KCl melt, $\times 330$, (d) powder obtained by firing granular synthesized material, $\times 45$.

Microstructural studies of piezoceramic powder obtained by firing granular synthesized material allow us to talk about the rounded shape of the particles (average diameter ~ 400 microns) and a relatively narrow distribution range (240–720 microns).

Based on the conducted studies of piezoceramic powders intended for use as a filler of a polymer matrix of composite materials with a type of connectivity 0–3, the following conclusions can be drawn.

Grinding in a ball mill of a highly porous ceramic material leads to the production of particles with a small average size

(~ 5 microns), close in size to the size of the ceramic grain and low structural perfection. Additional chemical treatment with HNO_3 solution makes it possible to increase the structural perfection of the powder by removing defective and impurity phases and narrow the particle size distribution interval due to the dissolution of the fine fraction and the destruction of fragmentation conglomerates. Subsequent annealing helps to eliminate inhomogeneous mechanical stresses that lead to the appearance of micro-deformations of the crystal lattice.

Additional heat treatment of the powder prepared by solid-phase synthesis under KCl melt makes it possible to significantly reduce the particle size interval. However, the pronounced diffusion of Ca^{2+} into the ionic melt leads to a violation of the stoichiometry of the chemical composition of the piezoceramic material.

The ceramic powder obtained by granulation of the synthesized material and subsequent high-temperature firing has the greatest perfection and rounded shape of the particles. The possibility of using a set of sieves allows you to adjust the particle size and the range of their distribution. The granulation technology used in the work allows particles to be obtained with tightly packed primary grains and high mechanical strength, and in this sense, it is preferable to spray drying granulation,⁶ that is, with a high density.

The direct introduction into the polymer of a synthesized powder intended for sintering high-density ceramics does not allow achieving high piezoelectric parameters of the composite material. First, such a powder has a small average particle size (~ 1 microns), and secondly, it is not single-phase. Earlier, we considered four methods of additional heat treatment of the synthesized powder and investigated the effect of technological techniques on the degree of perfection of the obtained particles, their shape and granulometric composition.⁴

Two types of piezoceramic filler were used in the preparation of composite materials: Powder with an average particle size ~ 5 microns obtained by crushing and grinding a porous ceramic frame, and granular powder with a maximum particle size ~ 250 microns. Composite materials with a degree of filling with a ceramic phase of 30–60% vol. were obtained by compression pressing. A mechanical mixture of ceramic powder and polymer was formed in the form of disks with a diameter of 15 mm and a height of 1 mm. For F-2ME, the molding temperature was 823–863°C, pressure 60–90 MPa, holding time at a maximum temperature of 0.25 h. For F-62, the molding temperature was reduced to 793–813°C. Ag electrodes were applied to opposite surfaces of disks by evaporation in vacuum. The samples were polarized in silicone oil with the application of a constant electric field with a voltage of 100–140 kV/cm at a temperature of 636–666°C, the exposure time varied from 0.5 to 2 h. Hydrostatic piezoelectric modules g_h , d_h and the reception factor $g_h \cdot d_h$ were calculated based on the sensitivity of the sample to sound pressure, measured by comparison in a small volume chamber at a frequency of 125 Hz using a sensitivity meter “Pascal-3C”.

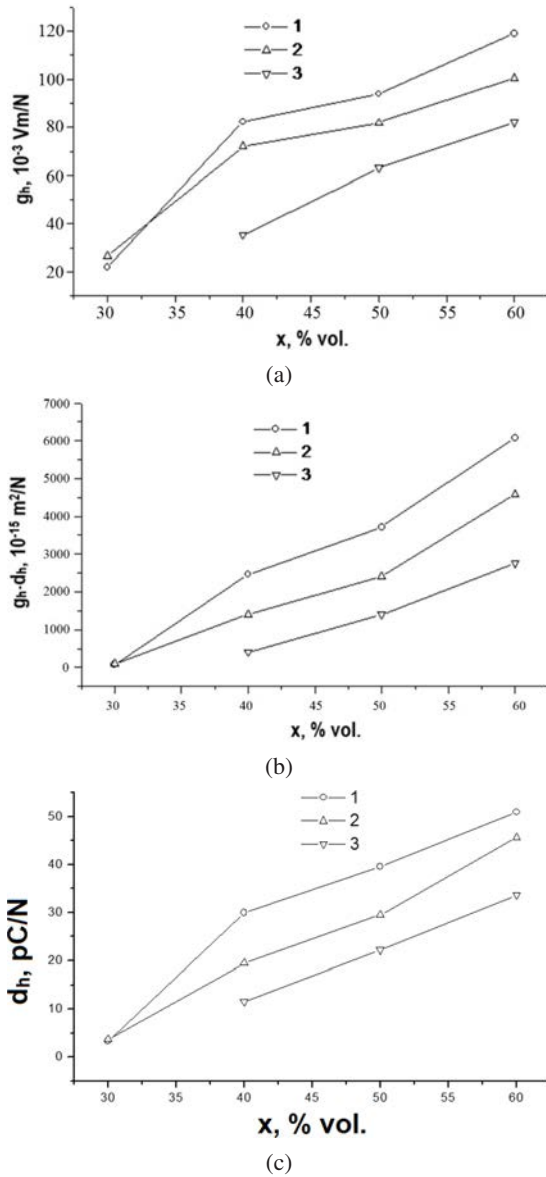


Fig. 2. Dependencies of the piezomodule g_h (a), the reception factor $g_h \cdot d_h$ (b) and the piezoelectric modulus d_h (c) on the degree of filling of the composite with ceramic powder: 1 – for polymer F-62 and granular powder; 2 – for polymer F-2ME and granular powder; 3 –for polymer F-2ME and fine powder.

Figure 2 shows the dependence of the piezosensitivity of g_h and the reception factor $g_h \cdot d_h$ on the degree of filling of the composite with ceramic powder for various polymer matrices and particle sizes. The maximum values of g_h and reception factor were achieved for F-62 with granular filler: $g_h = 119.1 \cdot 10^{-3} \text{ V}\cdot\text{m}/\text{N}$, $g_h \cdot d_h = 6074 \cdot 10^{-15} \text{ m}^2/\text{N}$ with a filling degree of 60% vol. For a composite based on F-2ME with the same degree of filling, these values were $100.4 \cdot 10^{-3} \text{ V}\cdot\text{m}/\text{N}$ and $4588 \cdot 10^{-15} \text{ m}^2/\text{N}$, respectively. The results obtained correspond to the best data from the foreign literature for composite materials ‘ceramics–polymer’ with the type of connectivity 0–3.^{5,6} The large values of piezoelectric

parameters of the composite based on F-62 can be explained by the high elastic malleability of the polymer matrix. The tendency to increase the piezoelectric modules of the composite with an increase in the average particle size of the ceramic filler is also confirmed.^{6–10} This effect can be caused by both the greater structural perfection of granular ceramic particles and the smaller specific surface area of the polymer–ceramic interface, i.e., the less shielding effect of charges concentrated at such boundaries.

The thickness of the studied samples is optimal from the point of view of the receiving sensitivity and the total output electrical impedance of the piezoelectric element used in hydroacoustic receiving devices.⁷ When ceramic particles are granulated by spray drying and processed by extrusion, composites based on F-62 and F-2ME can be used for mass production.

4. Conclusions

The analysis of the literature and patent data on piezoelectric composite materials ceramic–polymer with connectivity 0–3 is carried out. It is shown that the mass field of application of such materials is extended hydroacoustic linear and planar antennas, as a result of which the hydrostatic quality coefficient $d_h \cdot g_h$ should be used to optimize the functional parameters of the material. Solid solutions of the PT-CT system with zero values of piezoelectric modules meet the requirements for the ceramic component of the composite to the greatest extent and have advantages over other ceramic materials with high volume sensitivity such as PT and PT-VF.

It has been established that a polar polymer with high dielectric permittivity, low dielectric losses and no structural transformations in the operating temperature range is preferred as a polymer component. At the same time, the polymer must have good adhesion to the ceramic filler and be easily processed, in particular by extrusion. PVDF and a copolymer based on it — P(VDF-TrFE) — have become the most widespread.

It is concluded that the polarization conditions of composite materials with a type of connectivity 0–3 are mainly determined by the ratio of the resistivity of the polymer and ceramic phases. As a result, an increased polarization temperature and a long exposure time are used at the maximum achievable strength of the constant polarizing field. As a rule, only the ceramic phase is polarized. Polarization of the polymer component is possible only in the case of P(VDF-TrFE), mainly for film samples, and with the application of very high polarizing fields. This procedure is used to create composites with increased pyroelectric properties while suppressing piezoelectric parameters and vice versa.

Based on the analysis of the literature data and the results of our own experimental studies, it is shown that the value of the quality coefficient required for practical use is achieved in composite materials with a high degree of filling with the ceramic phase (50–65% vol.) and increases when the average

particle size approaches the thickness of the piezoelectric element. This is due to an increase in the number of mechanical and electrical contacts of piezoactive particles in the direction of polarization and a decrease in the thickness of the polymer layers between them. It is shown that the electroactive properties of a composite with connectivity 0–3 in the case when the bulk fraction of the filler exceeds 50% and/or the grain size is comparable to the thickness of the composite sample, can approach the properties of a two-phase composite system with connectivity types 1–3 and are described within the framework of a model assuming the presence of a mixed type of connectivity (0–3 and 1–3).

The role of various inclusions in the formation of effective dielectric and piezoelectric properties of composites based on PT–CT or PZT ceramics is analyzed within the framework of the new 0–3 composite “ceramics–polymer” model. It is shown that the ceramic component can be considered as a system of spherical and rod-shaped inclusions, and the polymer component as a homogeneous or heterogeneous medium. In the latter case, it is assumed that the polymer contains spherical inclusions with a vector of spontaneous polarization directed opposite to the vector of residual polarization of the matrix. Both rod-shaped ceramic inclusions and spherical polymer inclusions are shown to significantly affect the piezoelectric properties of composites PT–CT–P(VDF–TrFE) 75/25 mol.% in the range of volume concentrations of ceramics from 20 to 60 vol.%. This effect of two types of inclusions is associated with a relatively low piezoactivity of the ceramic component compared to polymer. In contrast, in composites based on PZT ceramics, which exhibit high piezoactivity compared to polymer, the main role in the formation of effective dielectric and piezoelectric properties in the concentration range from 20 to 60 vol.% is played by elongated (rod-shaped) ceramic inclusions.

The characteristics of the preparation of anisotropic piezoelectric ceramics based on solid solutions of the PT–CT system have been studied and the technology of synthesis and sintering of ceramics $\text{Pb}_{0.76}\text{Ca}_{0.24}(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}\text{O}_3$ has been developed. This ceramic has a maximum piezoelectric anisotropy, low permittivity ($\epsilon_{33}^T/\epsilon_0 = 200$) and low dielectric losses ($\text{tg}\delta = 1.5\%$), which makes it an optimal ceramic material for the formation of ceramic–polymer composite mixtures with high volume sensitivity.

The influence of technological factors on the structural perfection, shape and particle size of powders of anisotropic piezoelectric materials intended for use as an active component of composites with a type of connectivity 0–3 is considered. Four methods of additional heat treatment of the synthesized powder have been studied. Optical microscopic and X-ray examination of powders obtained by various methods was carried out, as a result of which it was established that the ceramic powder obtained by granulation of the synthesized material with subsequent high-temperature firing has the greatest perfection and the rounded shape of the particles.

Further studies of volume-sensitive piezoelectric composite materials “ceramics–polymer” with a type of connectivity 0–3 should primarily be aimed at improving the technology of composite preparation:

- increasing the uniformity of the distribution of ceramic filler in the polymer matrix due to the dissolution of PVDF-based fluoropolymers in aprotic solvents and subsequent homogenization of the suspension of ceramic particles in solution;
- using the spray drying method to obtain spherical ceramic particles with a given average size and a small dispersion of the size distribution;
- improvement of the technique of applying a metallized coating to a composite in order to prevent its burnout during polarization;
- the use of the polarization method in the corona discharge, or the use of stepwise polarization with cyclic voltage removal and cooling in order to increase the strength of the polarizing field.

Of considerable interest is also the study of the frequency dependence of dielectric permittivity and dielectric losses, as well as the study of nonlinear behavior under high mechanical loads. The presence of the ceramic–polymer interface should have a noticeable effect on the frequency spectrum of dielectric parameters. The study of the dielectric properties of unpolarized and polarized composites in a wide frequency range with varying degrees of filling can provide information on the “slow” processes of polarizability and highlight the contribution of various mechanisms of polarizability. The results obtained can be used to determine the optimal polarization modes and to evaluate the frequency dependence of the functional parameters of piezoelectric converters made of composite materials.

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