

A new composite piezoactive material for additive technologies based on stereolithography

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A new piezoactive composite material based on the "polymer–porous piezoceramics" system has been developed, in which a ultraviolet curable photopolymer resin is used as the matrix. The material exhibits high values of the longitudinal piezoelectric modulus and is suitable for use as a working material in the fabrication of active elements using ultraviolet stereolithography technology. The results of investigations into the electromechanical properties of the material are presented.

Keywords: piezoactive composite, porous piezoceramics, photopolymer resin, additive technologies, stereolithography.

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Additive technologies have recently become widespread and are used in several economic sectors, such as medicine, construction, powder metallurgy, etc. [1]. A possibility emerges in this context to adapt certain additive technologies for three-dimensional printing of piezoactive elements for the purpose of increasing the production efficiency and cost reduction. The engineering of new piezoactive materials and adaptation of existing additive technologies for their production open up new prospects for the fabrication of more efficient and functional piezoelectric elements. Piezoactive materials research may enable the development of new innovative products, such as advanced sensor devices, active elements for acoustic systems, medical devices, etc. In addition, the use of additive technologies for fabrication of piezoactive elements will help improve the quality of products, enhance their technical characteristics, and reduce production time. Therefore, progress in this area may lead to the emergence of more efficient and innovative technologies for production of piezoactive materials, which will add to their marketability and improve the quality and efficiency of various devices and systems with piezoelectric elements.

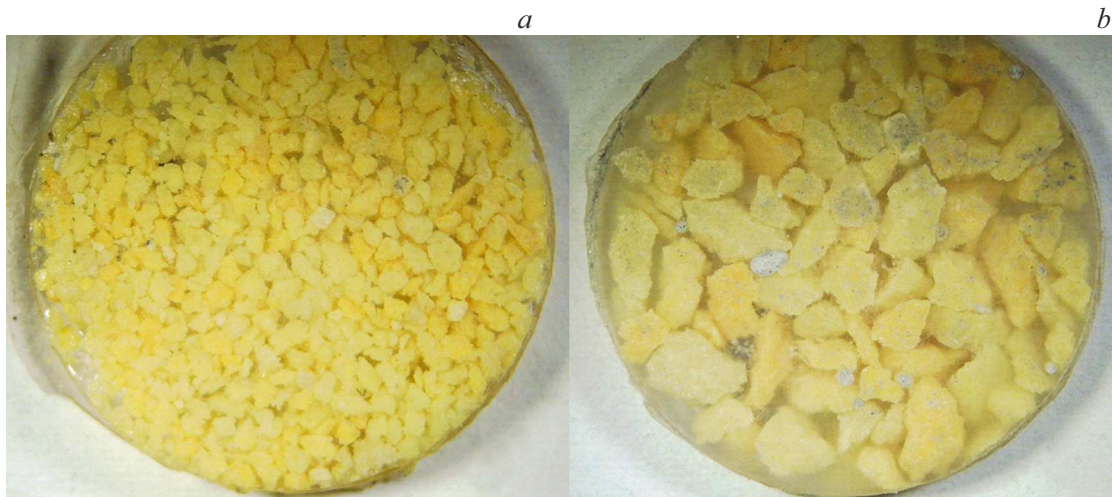
When analyzing literature data, one first needs to note the developments in the field of printing with semi-fused polymer filament (FDM/FFF method), where polyvinylidene fluoride, which features a piezoelectric effect, is used as the working polymer material. However, its piezoelectric modulus d_{33} has a value on the order of 30 pC/N. It has been reported [2,3] that certain modifications of this material provide an opportunity to raise its piezoelectric modulus to 100 pC/N. The technique of selective laser printing (SLM method) [4], which is one of the few additive technologies that allow for the production of ceramics, is also promising. In addition, we have worked on a piezoceramic–polymer composite that may be used as a working material for layer-

by-layer bonding of powders [5,6]. This technique is distinguished by the lack of any significant restrictions on the size of powder particles, enabling the use of piezoactive particles of macroscopic sizes (up to 3–5 mm). This provides an opportunity to produce piezoelectric elements with a small number of layers (down to a single layer) of piezoactive particles. Thus, it becomes possible to produce composite materials with piezoelectric moduli close in magnitude to the piezoelectric moduli of the original piezoelectric ceramics.

Another additive technology allowing for the use of macroscopic piezoceramic particles is layer-by-layer stereolithographic exposure of UV-sensitive resins (SLA/DLP method). It is characterized by a high stability of product shape, which is maintained even when working with composite materials. This is attributable to the fact that the technological suitability of the composition is governed by a relatively small number of factors, which include viscosity and optical transmittance in the ultraviolet range (365–405 nm).

Despite the difficulties associated with the effects of reflection and refraction by added particles, their sedimentation, and the resulting intrastructural defects and interlayer delamination, this technology is one of the potential avenues for development of the concept of piezoactive polymer-based composites [7]. For example, certain resins may be cured effectively to a depth of up to 2 mm, which is comparable to the thickness of active elements of commercially available piezoceramic transducers. This makes it possible to apply this technology to the fabrication of single-layer composite piezoelectric elements with large millimeter-sized ceramic particles, which may prove efficient in working with materials based on the lead zirconate titanate (PZT) system.

In this context, the aim of the present study is to examine the possibility of creating a piezoceramic–polymer compos-



Elements made from the porous piezoceramic–photopolymer composite photographed after grinding but before the application of electrodes. *a* — Composite with 0.5–1.0 mm ceramic particles; *b* — composite with 1.0–2.0 mm ceramic particles. The diameter of disks is 20 mm.

ite that would be produced using the additive technology of UV stereolithography, have piezoactive properties, and feature macroscopic particles of porous piezoceramics and a UV-curable photopolymer resin serving as piezoactive particles and a polymer binder, respectively.

Porous piezoceramic particles were used as the piezoactive component in the composite [8]. It should be noted that this refers not to the natural porosity of the ceramic material introduced inevitably in the process of its production. The piezoceramic material used here was deliberately produced with predetermined pore sizes and concentrations. This technique was developed at the Southern Federal University [9]. Piezoceramic particles in the composite were the particles of porous piezoceramics PZT-19 of the following composition: $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 1\% \text{Nb}_2\text{O}_5$ [10]. This is the most common piezoelectric material produced in Russia that provides balanced electromechanical properties and is used widely in industry (in particular, in the fabrication of ultrasonic transducers and other devices).

Its initial porosity was 30%, and the average pore size was $50\mu\text{m}$. Particles of two form factors were used: 0.5–1.0 and 1.0–2.0 mm. Sieves with cell sizes of 0.5, 1.0, and 2.0 mm were used to select particles. The use of porous piezoceramic particles instead of conventional ones provides a number of decisive technological advantages for piezoceramic–polymer composites, since, first, it eliminates the need to use diamond instruments for mechanical processing of samples, which is extremely difficult given the presence of a polymer binder. Second, the mechanical parameters, such as density and sound velocity, of porous ceramics may be controlled via the adjustment of their porosity, enabling acoustic matching of polymer and ceramic components of the composite.

Transparent photopolymer Anycubic High Clear resin was chosen to be used as a polymer binder based on the results presented in [11,12]. The samples were shaped into

cylinders with a diameter of 22 mm and a height of 1.5 mm in open collapsible matrices made of transparent sheet polyethylene. The required powder additive mass (1.6 g) was calculated based on a solid fraction of 50 vol.%; ceramic and resin densities of 5.6 and 1.15 g/cm^3 , respectively; and a mold volume of 0.57 cm^3 . Particles were introduced into the matrix and distributed evenly along the bottom using a scraper, and the working volume was then filled with an excess amount of resin. A scraper was also used to remove excess resin from the surface. The composite was cured by illuminating both ends of the cylinder with two ultraviolet lamps consisting of six diodes with a total power of 6 W. To facilitate removal after curing, the samples were outlined additionally with radiation of a pulsed fiber laser with a wavelength of 1065 nm, a power of 30 W, and a pulse rate of 30 kHz. The calculated density of the samples was 3.38 g/cm^3 . Electrodes in the form of a conductive nickel-based paste were applied to flat surfaces of the samples. The samples were polarized in air at a temperature of 423 K and a constant electric field strength of 1 kV/mm. The coercive field strength for this material was 900 V/mm at a temperature of 293 K. Its magnitude decreased with increasing temperature. The photographic image of composite samples without electrodes after grinding is presented in the figure. The piezoceramic particle content after grinding was 50 vol.%.

The main electrophysical and electromechanical parameters of the obtained composite samples and the original piezoceramic materials are listed in the table. Here, ε is the relative permittivity, d_{33} is the longitudinal piezoelectric modulus measured quasi-statically, g_{33} is the piezoelectric constant that characterizes the sensitivity of the material and is equal to the ratio of piezoelectric modulus d_{33} to permittivity $\varepsilon\varepsilon_0$, and K_t is the coefficient of electromechanical coupling of the thickness oscillation mode.

Comparison of parameters of the original piezoceramics and the obtained composites

| Designation | ε | d_{33} , pC/N | g_{33} , mV · m/N | K_t |
|--|---------------|-----------------|------------------------|-------|
| PZT-19 | 1600 | 340 | 24.0 | 0.48 |
| PZT-19 with a porosity of 30 % | 1150 | 350 | 34.4 | 0.55 |
| Composite with particles with a size of 0.5–1.0 mm | 48 | 60 | 141.2 | — |
| Composite with particles with a size of 1.0–2.0 mm | 105 | 130 | 140.0 | — |

The table makes it evident that the permittivity of the composite samples was an order of magnitude lower than the permittivity of the original material. At the same time, piezoelectric modulus d_{33} decreased by a factor of 3–5 only. The composite was also characterized by a virtually complete lack of piezoelectric resonances, which made it impossible to measure certain electromechanical characteristics, such as the electromechanical coupling coefficient. This may be attributed to the presence of horizontal polymer interlayers between piezoceramic particles that partially prevent direct mechanical contact of these particles with the electrodes. At the same time, owing to a huge difference in relative permittivity between the polymer binder ($\varepsilon = 3$) and porous piezoceramic particles ($\varepsilon = 1150$), the polymer interlayers do not allow the electric field to penetrate into piezoceramic particles. This produces a polarization gradient within the samples, exerting a negative influence on both the piezoelectric properties and the resonance properties of the composite. A significant mismatch of acoustic resistances of the composite components also contributes to the suppression of piezoelectric resonances. At the same time, a combination of sufficiently high piezoelectric modulus values and low permittivity ensures very high values of piezoelectric constant g_{33} that characterizes the sensitivity of the piezoelectric material operating as a detector of mechanical vibrations. The practical lack of mechanical resonances of the material allows one to use it in active elements for broadband detectors of ultrasonic waves.

Thus, it can be stated that it is possible to produce a composite material based on a photopolymer resin and macroscopic particles of porous piezoceramics that features piezoelectric properties and may be used as a working material in the production of piezoelectric elements by additive UV stereolithography. With its unique properties, this piezoactive material may serve as a basis for highly efficient piezoelectric devices, such as broadband ultrasonic detectors, piezoelectric energy generators, seismic detectors, etc. The results of examination of its electromechanical characteristics suggest that it holds promise for industrial application in the field of electronics and mechatronics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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