MAGNETOELECTRIC RESPONSE OF A POLYMER COMPOSITE FILLED WITH A MIXTURE OF $CoFe_2O_4/BaTiO_3$ PARTICLES

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Abstract. We studied the magnetoelectric response of a composite material based on a rubber-like polymer filled with submicron-sized cobalt ferrite and barium titanate particles. Using a computer experiment, the dependence of the magnetoelectric response of a representative volume of such a composite on the system parameters is studied. Based on the results of the computer experiment, methods for enhancing the magnetoelectric response of such composites are proposed.

Keywords: *computer experiment, magnetoelectric effect, multiferroic composite*

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INTRODUCTION

Multiferroics is a class of materials in which there are at least two types of ordered states: ferromagnetic and segmentoelectric or ferroelastic [1-3]. When both ferromagnetic and segmentoelectric orders are combined in the structure of a material, this gives it magnetoelectric (ME) properties. Indeed, the application of an external magnetic field changes the electric polarization of such a system, while exposure to an electric field causes it to change its magnetization. These two types of response are known as the forward and reverse ME effect.

Currently, much attention is paid to the development of new composite multiferroics with enhanced ME effect. In terms of the latter, composite systems surpass single-phase multiferroics by several orders of magnitude, because of the strong mechanical coupling between the segmentoelectric and ferromagnetic phases [1, 4-6]. The advent of composite ME materials has made it possible to create high-quality magnetic and electric field sensors [7-12], including those for biomedical applications [13, 14] and for "energy harvesting" [7,15,16]. Thus, the ME effect stimulated by an alternating field has found its application in "smart" substrates accelerating the differentiation of stem cells [12].

Various methods are used in the fabrication of ME composites. One of the most common ones is bonding of plane-parallel plates of ferromagnetic and segnetoelectric materials [1]. Another method is sintering of a mixture of micro- and nanoparticles placed in a polymer matrix [1,2,17]. Each of these methods has its own advantages and disadvantages. The first method is easy to implement and allows obtaining high values of the ME response; its disadvantages include, in particular, the limited shape of the finished samples, since they should be only plane-parallel plates. The second method gives lower values of the ME effect, but its advantage is the absence of restrictions on the shape of samples [1].

Despite the fact that the ME effect in polymer composites is obviously lower than in ceramic composites, it is by no means weak. On the other hand, an important advantage of polymer composites is their ease of fabrication, flexibility, and ease of processing [2,17]. In addition, polymer interfaces are characterized by good biocompatibility. Together, these advantages make them a unique tool for a number of biomedical applications where it is required to utilize the ME effect. For example, to create surfaces for the cultivation of bacterial strains on which controlled electrical charges and mechanical stresses are remotely generated by applying an external magnetic field [18,19]).

In the fabrication of ME composites, it is necessary to take into account a number of factors: type, size and concentration of ferromagnetic and segmentoelectric particles, mechanical properties of the matrix and others [20]. To predict the properties of such complex multicomponent media, computer modeling is probably the best current approach [2, 21].

Modern computer experiments that are used to study polymer multiferroics include, for example, the virtual spring method [2] (which has proven itself for the description of magnetically active elastomers) and the finite element method [22]. Full-scale numerical modeling of polymer multiferroics involves the consideration of large ensembles of particles and, consequently, the use of very large computer resources [2, 3, 6, 15, 21, 22]. However, modeling of systems with a relatively small number of particles can - at least on a qualitative level - advance the understanding of how the response of a composite DOE to an applied field is formed. In the present work, a system with three submicron-sized particles, of which two are ferrimagnetic (cobalt ferrite) and one is segmentoelectric (barium titanate), is considered as an example of a representative volume of such a composite.

The main subject of the study is the dependence of the direct ME effect in a representative volume of a multiferroic composite on the mutual arrangement of phases and the orientation of their light axes: magnetization for ferromagnetics and polarization for segmentoelectric. The elastomeric matrix is considered to be a linear-elastic incompressible continuum with Young's modulus = 1 MPa).

THEORETICAL MODEL

Since the particle sizes are much larger than the sizes of individual molecules, a mesoscopic approach is used to describe the composite material, i.e., the composite is represented by a system of particles immersed in a continuous medium, the matrix.

The particles are assumed to be ideal incompressible spheres (circles, since the problem formulation is two-dimensional) with a high modulus of elasticity (of the order of units GPa). The size of ferromagnetic particles is taken to be 5-10 times smaller than the size of a segmentoelectric particle. Since the Young's moduli of the matrix and particles differ by several orders of magnitude, it is quite acceptable to use the linear theory of elasticity for calculations [22].

In the two-dimensional formulation, as already mentioned, the matrix is defined in the form of a rectangle, the size of which is much larger than any total size of all three particles; the particles themselves are located as far as possible from the boundaries of the matrix. One (conventionally, the bottom) side of the matrix is rigidly fixed, the other boundaries are free.

The formulation of the problem implies that the ferrimagnetic and segmentoelectric particles, as well as the matrix, consist of incompressible matrices; the adhesion of particles of both genera to the matrix is assumed to be absolute. It is assumed that both ferrimagnetic and segmentoelectric particles are in a single-domain state. In this case, ferrite particles are considered to be magnetically rigid, i.e., the change in the orientation of their magnetic moments occurs only together with the change in the orientation of the particle itself. Neither magnetostriction of ferrite particles nor spontaneous polarization of segmentoelectric particles is taken into account. The quasi-static formulation of the problem is applied, i.e., it is considered that the establishment of equilibrium values of stationary thermodynamic parameters occurs much faster compared to the characteristic time of change of the external magnetic field. This field is homogeneous and quasi-stationary, the external electric field is absent.

Let us consider the relation relating the induced electric polarization to the applied mechanical stress, the form of this relation is given in [23]:

$$D_i = D_{i0} + \varepsilon_{ik} E_i E_k + 4\pi \gamma_{ik,l} \sigma_{kl}, \qquad (1)$$

here$\vec{D}$ is the electric induction vector,$\vec{E}$ is the electric field vector inside the sample,ε_{ik} is the dielectric constant tensor of the sample,$\gamma_{ik,l}$ is the piezomodule tensor.

Since the direct ME effect in the composite arises due to the mechanical effect of the ferromagnetic phase on the segmentoelectric phase [6], it is sufficient to limit the modeling of the direct ME effect by considering only the third summand in equation (1):

$$D_i^{(\text{stress})} = 4\pi \gamma_{ik,l} \sigma_{kl}. \qquad (2)$$

Relationship (2) can be written in the vector form adopted in piezoelectric physics:

$$D_i^{(\text{stress})} = 4\pi d_{ik} t_k, \qquad (3)$$

where d_{ik} is a component of the rectangular matrix 3× 6, which (matrix) is a representation of the piezomodule tensor, t_k is a component of the 6-dimensional vector

$$\vec{t} = (\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23} = \sigma_{32}, \sigma_{13} = \sigma_{31}, \sigma_{12} = \sigma_{21}), \tag{4}$$

which can be replaced by the mechanical stress tensor due to the symmetry of the latter. Such representation of formulas (3) and (4) is used, for example, in [4, 15, 16].

According to [24], in barium titanate single crystals, the matrix d_{ik} has the following form:

$$d_{ik} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}. \tag{5}$$

When passing to the two-dimensional formulation, let us direct the light polarization axis along Oy and take into account relation (5). This gives

$$P_1 = d_{15}\sigma_{12}, \qquad P_2 = d_{31}\sigma_{11} + d_{33}\sigma_{22}. \tag{6}$$

Thereby, the relationship between mechanical stress and polarization vector has been established through the piezomoduli of barium titanate.

Let us specify the relations to which the variables of the problem obey. In the approximation of point dipoles, the magnetic interparticle interaction is described by the potential

$$U_{ij}^{(dd)} = \frac{(\vec{m}_i\vec{m}_j)}{r_{ij}^3} - \frac{3(\vec{m}_i\vec{r}_{ij})(\vec{m}_j\vec{r}_{ij})}{r_{ij}^5}, \tag{7}$$

where $\vec{m}$ is the magnetic moment of the particle, $\vec{r_{ij}}$ is the radius-vector of the distance between their centers.

In the adopted formulation of the DOE problem, the composite is a continuous medium with different regions, each of which is characterized by its own set of material parameters. Therefore, to describe the mechanical properties of such a medium, we will use the fact that the stress tensor obeys the equilibrium equation at all points of the specimen and at all interfaces:

$$\mathrm{Div}\,\sigma_{ik} \equiv \frac{\partial \sigma_{ik}}{\partial x_k} = 0. \tag{8}$$

Since the elastic modulus of the matrix is sufficiently large, its relative deformations in the considered range of fields are small, so that it is acceptable to use the isotropic Hooke's law [25] to describe the mechanical behavior:

$$u_{ik} = \mu_{iklm}\sigma_{lm}, \qquad u_{ik} = \frac{1}{2G}\left(\sigma_{ik} - \frac{1}{3}\sigma_{ll}\delta_{ik}\right) + \frac{1}{9K}\sigma_{ll}\delta_{ik}, \tag{9}$$

whereμ_{iklm} is the general form of the linear ductility coefficient tensor,G is the shear modulus,K is the modulus of all-round compression. Let us derive the components of the stress tensor from (9):

$$\sigma_{ik} = \lambda_{iklm}u_{lm}, \qquad \sigma_{ik} = 2Gu_{ik} + \left(K - \frac{2}{3}G\right)u_{ll}\delta_{ik}; \tag{10}$$

hereλ_{iklm} is the elasticity modulus tensor.

To solve the problem of the quasi-static ME effect, we used the method of minimizing the free energy functional of the system. Let us obtain an expression for this functional with respect to the system under consideration. According to [18], the incremental free energy of a piezoelectric can be represented as

$$dF = -SdT + \sigma_{ik}du_{ik} - \frac{1}{4\pi}\vec{D}d\vec{E}, \tag{11}$$

where$S$ is entropy and$T$ is temperature. Since in the problem formulation there is no external electric field, the expression (11) transforms to

$$d\tilde{F} = -SdT + \sigma_{ik}du_{ik}. \tag{12}$$

Substituting equation (10) into equation (12) and integrating, we obtain the following expression for the free energy functional of the system without taking into account the energy of dipole-dipole interaction of ferromagnetic particles:

$$\tilde{F} = F_0 + G(u_{ik})^2 + \frac{1}{2}\left(K - \frac{2}{3}G\right)u_{ll}^2. \tag{13}$$

Since an isothermal situation is considered, the summandF_0 in equation (13) is a constant value that does not need to be taken into account in minimizing the functional. In this case, adding the magnetic energy to (13), we have

$$\tilde{F} = G(u_{ik})^2 + \frac{1}{2}\left(K - \frac{2}{3}G\right)u_{ll}^2 + U_{ij}^{(dd)}. \tag{14}$$

For convenience of modeling, the functional (14) should be disproportioned. It is convenient to choose the value$G$, i.e., the shear modulus of the matrix, as the scale of the energy density (modulus of elasticity). After such dismeasurement, the functional (14) is minimized and the electric polarization of the composite is calculated from the obtained solution using expression (6).

Let us describe the input parameters, which served as input data of the performed calculation. The geometrical scheme of the system under consideration is shown in Figure 1. As indicated above, dense rubber with a shear modulus of$G = 1$ MPa is taken as a matrix. The ferrimagnetic phase has the characteristics of cobalt ferrite, and the segmentoelectric phase corresponds to barium titanate in its properties. Both of these ceramics have Young's modulus on the order of 100 GPa. The spontaneous magnetization of cobalt ferrite particles is assumed to be 2500 A/m [19]. The diameters of the ferrimagnetic and segnetoelectric particles are 0.5 μm and 3 μm, respectively; the gap between the ferromagnetic and segnetoelectric particles is 0.5 μm; and the matrix dimensions are 12 by 24 μm. Such dimensions of the matrix are necessary to minimize the influence of the matrix-vacuum boundary.

The Python programming language was chosen to implement the program code. The solution of differential equations by the finite element method was performed using the dolfin package. The mshr package was used for geometry construction and mesh generation.

COMPUTER EXPERIMENT RESULTS

The calculation was carried out for a magnetic field in the range of 0 to 1 Tesla, which covers almost all real scenarios of the use of ME composites. Material parameters of phases (they are partially specified above) were chosen according to literature data.

In the course of the computer experiment, the linear character of the dependence of the polarization of the segmentoelectric particle over the entire range of the magnetic field was established. To save computational resources, small values of the magnetic field - 50 mTl - were used in the study of the dependence of the ME response on various parameters of the system, since it requires multiples fewer iterations to achieve it than to achieve fields of units of Tl with equal field increment. In numerical experiments where the dependence on the particle magnetization was not studied, its value was 2500 A/m (the direction is always along the axis).Oy

As can be seen from Fig. 2a, the dependence of the polarization of the segmentoelectric particle depends weakly on the gap between the segmentoelectric and ferromagnetic particles in the selected range of gap values. Thus, when the gap is increased by 20 times, the drop of the polarization component of the segmentoelectric particle is only about 10%, and the dependence of$y$ -component of polarization is practically absent. The predominance of the x-component *of* polarization is also observed, which is explained by the predominance of shear stresses, as can be seen from expression (6). Consequently, our results show that the main mechanism of ferromagnetic particles impact on the matrix in this case is rotation.

As can be seen from Fig. 2b, the dependence of the *x-component of* the polarization of a segmentoelectric particle on the magnetization of ferromagnetic particles is linear, and the changes in$y$ -component are small. The predominant magnitude and linearity of the field dependence of the x-component is explained, of course, by the fact that Zeeman energy is linear in the magnitude of the field. Indeed, the *x-component* of polarization arises due to shear stresses that create ferromagnetic particles on which act magnetic moments$(\vec{m} \times \vec{B})$ linear in the field.

As Fig. 2c shows, the x-component *of* the polarization of a segmentoelectric particle depends nonlinearly on the radius of ferromagnetic particles. It is reasonable to assume that this nonlinearity, resembling a parabola, is due to the quadratic (in two-dimensional formulation) growth of the magnetic moment as the particle radius changes.

The influence of the collective effect (dependence on the configuration of the ferroparticle pair) is illustrated in Fig. 2g. The maximum of the ME response is reached at the value$\alpha = 180°$ (see Fig. 1), i.e., in the case when the pair of ferroparticles is located along the direction of the applied field on different sides of the segmentoelectric particle.

CONCLUSION

It can be seen from the obtained dependences that the magnitude of the direct ME effect at given material parameters of the composite phases and composite configuration is determined by the rotation of ferromagnetic particles, i.e., by shear stresses. Shear stresses induce in the segmentoelectric particles the *x-component of* polarization, whereas the light axis of polarization, and hence the spontaneous part of polarization, is directed along the axis Oy . It follows that such a contribution not only increases the polarization of the particle, but also changes the direction of polarization, which should be taken into account when using such a material. It is also worth noting the weak dependence of the magnitude of the ME effect on the distance between the particles, which can, at first glance, be interpreted as a weak dependence of the magnitude of the ME response on the concentration of segmentoelectric and ferromagnetic fillers. However, this conclusion cannot be fully proved, taking into account the small number of particles in the considered system. Indeed, it is possible to judge the dependence of the ME response on such a characteristic as concentration only in a computer experiment, i.e., by studying a large ensemble of particles. Therefore, the obtained result can only be an indication of the possibility of such a hypothesis, which has yet to be verified by computer modeling and field experiments.

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FIGURE CAPTIONS

Fig. 1. Schematic representation of a representative volume. Hereinafter: 1 - segmentoelectric particle, 2 - ferromagnetic particles, 3 - electroneutral matrix,$\vec{M}$ - magnetization of ferromagnetic particles,R_p - radius of segmentoelectric particles,R_m - radius of ferromagnetic particles,$\vec{P}$ - light polarization axis of segmentoelectric particle, r - gap between ferromagnetic particle and segmentoelectric particle.

Fig. 2. Dependence of the *x* and *y* components of the polarization$\vec{P}$ on: the gap between ferromagnetic and segmentoelectric particles (a); the particle magnetization (b); the radius of ferromagnetic particles (c); the angle α (see Fig. 1) (d).

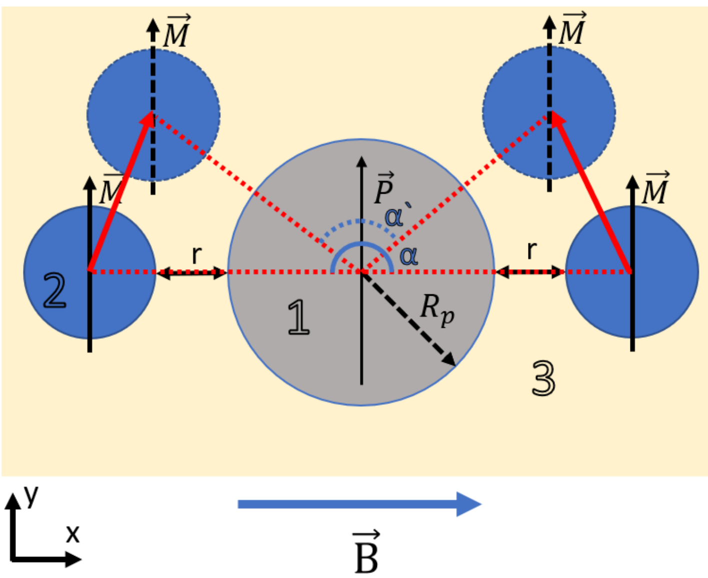
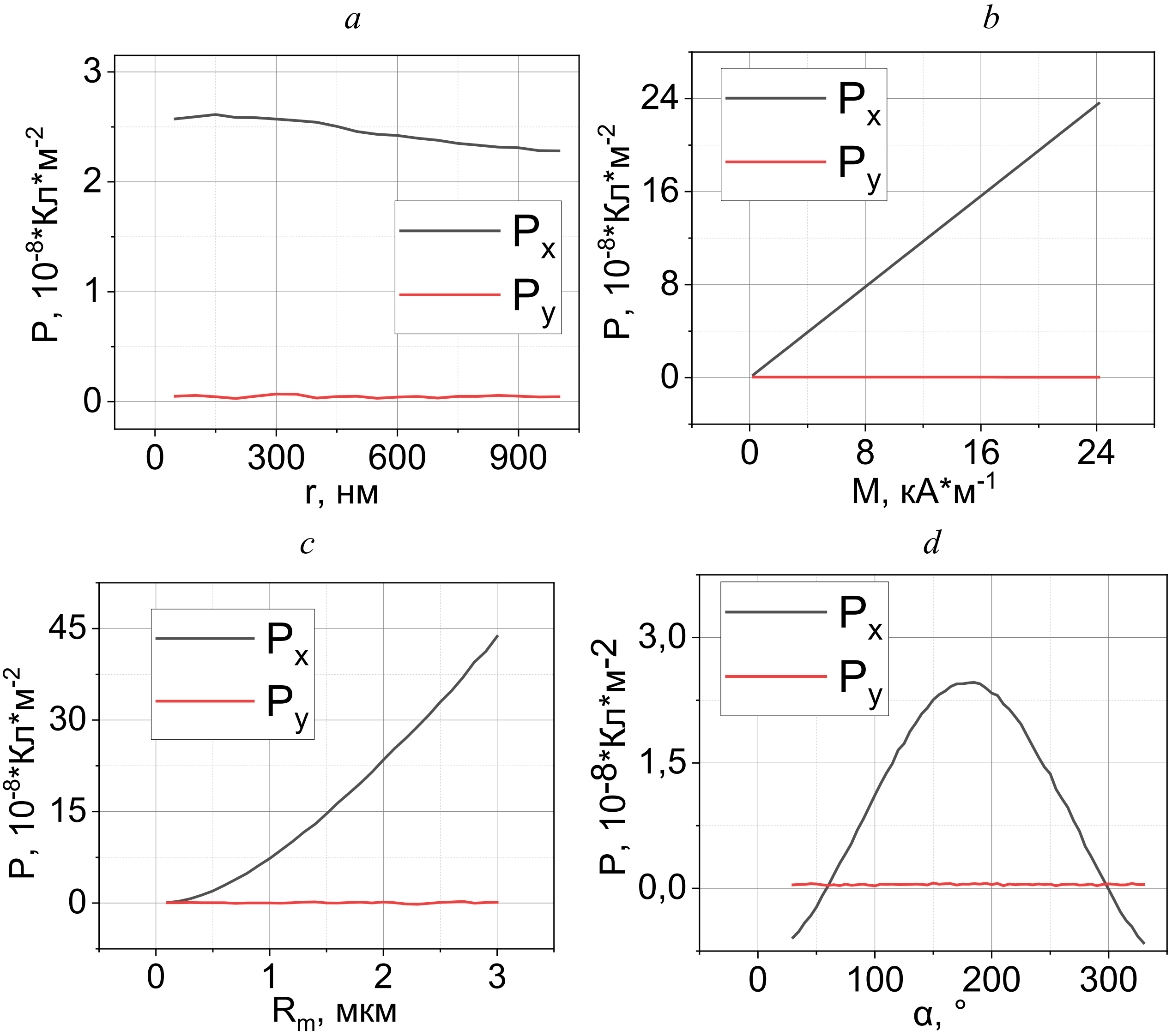


Fig. 1.


a
P, 10-8*Кл*м-2
3
2
1
0
0
300
600
900
r, нм
Px
Py
b
P, 10-8*Кл*м-2
24
16
8
0
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16
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M, кА*м-1
Px
Py
c
P, 10-8*Кл*м-2
45
30
15
0
0
1
2
3
Rm, мкм
Px
Py
d
P, 10-8*Кл*м-2
3,0
1,5
0,0
0
100
200
300
α, °
Px
Py

Fig. 2.