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Theoretical design of high-performance polymer-based magnetoelectric of fibrilar structures

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ABSTRACT

Low-dimensional magnetoelectric (ME) materials are attracting high attention both from the scientific and technological communities due to their interesting electrical, optical and mechanical properties allied to their novel applications in micro and nano smart-devices, drug delivery platforms, heterogeneous catalysis, tissue engineering, biosensors and bio-actuators, among others. Once the low dimensionality of these materials complicate the direct measurement of their performance at a large range of magnetic fields and high filler contents, this work theoretically evaluates low dimensional ME structures from spherical to ellipsoidal and fibre-shaped. The structures are based on $CoFe_2O_4$/poly(vinylidene fluoride) composites and the simulations are performed through the finite element method (FEM).

Results for 50 wt percentage (wt.%) $CoFe_2O_4$ content samples reveal ME coefficients of 182 V/cm at 684 Oe for the spheres and 4241 V/cm at a magnetic field of 208 Oe on the medium eccentricity (of 1200) ellipsoidal structure. These fibre shaped ellipsoids exhibit higher ME values than the spheres and the axisymmetric fibres: 1601 V/cm at 30 Oe for an ellipsoid with eccentricity of 3200. Further, the fibrilar structure strongly decreases the ME performance and operational magnetic field to 14.7 V/cm at 1.38 Oe.

These results establish the potential and limits, in terms of magnetic field and electric response, of the use of these composites and structures on technological ME device applications. Further, it demonstrates that suitable tuning of shape and dimensions allow to strongly increase ME response of the composites.

1. Introduction

The evolution of technology increasingly demands size reduction and more accurate and powerful performance of devices [1]. The innovation in such devices is possible thanks to the investigation, optimization and production of new materials. The development of high performance smart materials is particularly important for sensors and actuators [2,3]. Multiferroics, smart materials which exhibit two or more ferroic properties, which include ferroelectricity, ferromagnetism and ferroelasticity, deserve special attention due to their attractive physical properties and large potential for technological applications. However, what makes multiferroic materials scientifically and technologically particularly interesting is not only their ability to display multiple order states but, most importantly, the cross coupling effects that can occur between these order states such as the magnetoelectric (ME) effect [4,5].

On a ME material, the application of a magnetic field influences the polarization of the material, and inversely, an electric field will result in a magnetization of the material. This coupling is, in some cases such as ME composites, generated indirectly via stress/strain within the material. This ME response is often described by the ME coefficient (α_{ME}), as [6]:

$$\alpha_{ME} = \frac{\delta P}{\delta H} \quad (1)$$

where α_{ME} represents electrical polarization variation, *P*, induced by the application of a magnetic field, *H*.

Single-phase materials, in which ferromagnetism and ferroelectricity independently appear are rare [7], show low ME coupling at low temperatures and low Curie temperatures [8]. To overcome those limitations, ME composites have emerged as a solution. Magnetostrictive (MS) and piezoelectric (PE) phases

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within a composite allow an improved ME response. A high number of applications have been developed on this principle [9], including magnetically controlled electro-optic devices, microwave phase shifters (electrically controlled), broadband magnetic field sensors and memory devices, among others. Strong efforts have been thus invested on enhancing the ME coupling to achieve higher values than those obtained by single phase materials [10].

Such ME composite materials can be ceramic-based or polymer-based, and although ceramic-based materials achieve ME coefficients up to three orders of magnitude higher than polymer-based ones, they present limitations due to reactions at the interfacial regions, high dielectric losses and low stability on device applications [5,6]. Polymer-based ME materials overthrow this difficulties, with strong strain coupling, flexibility with low leakage currents, shaping feasibility, low temperature fabrication and low cost, obtaining for those features high industry interest [11].

Regarding structure, fibrilar and sphere forms present several advantages for specific applications due to larger area to volume ratio, when compared to traditional structures, such as nanocomposites and laminates [12]. Further, they show unusual electrical, optical and mechanical properties [13,14] and, when biocompatible, found application in biomedical applications such as drug delivery platforms, tissue engineering, biosensors and bioctuators [15–17]. Some polymer-based ME fibrilar structures have already been reported and the followed experimental procedure can be found in Ref. [18].

Despite all these benefits and innovation opportunities, the specific features of fibres and spheres, typically at the micro or nanoscale, complicate the direct measurement of their performance at a large range of magnetic fields and high particle concentrations. In fact, the experimental determination of the ME response was made in terms of the variation of the piezoelectric response and only for just one magnetic field value, 1000 Oe in the case of fibres and 2200 Oe in the case of spheres [19]. Additionally such measurements based on the piezoelectric response change have some disadvantages such as the accumulation of induced charges at the electrodes that influence the output and the impossibility of studying the ME response as a function of the frequency and magnetic field intensity, key features on the incorporation of ME materials in micro and nanodevices [20,21]. This brings the attention to the integral knowledge of the functioning of such low dimensional structures, and its component materials, in order to understand their way to operate. Developing mathematical models and simulations that allow this understanding has become essential in the generation of new technologies that enable achieving smaller and enhanced dispositives [22]. In this way, such mathematical models and simulations promote this know-how in order to proper understand, tailor and predict composite performance and to design improved and smaller devices [23].

Regarding the theoretical modelling of ME composites, phase field-type models are usually applied to layered and particulated composites by coupling thermodynamic evolution equations with respect to magnetization and polarization [24]. Another phenomenological phase field modelling approach by computing the magnetic domain structures evolution of magnetostrictive phase [25]. By modelling the magnetoelastic energy was possible to combine physical rigor with relatively simple treatment that successfully simulated inverse effect of magnetostriction in magnetoelectric laminates.

Later, a micromechanics-based averaging of a representative volume element with finite element (FE) analysis were used to study the effective mechanical, magnetic, dielectric, and ME properties of an electro-magneto-elastic material with piezoelectric and piezomagnetic fibres as functions of each phase volume fractions [26].

The electromechanically coupled boundary value problems such as the ones observed on ME nanocomposites were evaluated by using a direct micro-macro transition procedure FE^2-method that was created on the FE theoretical solution of a macroscopic value problem at boundary regions [27].

In Ref. [16], a general framework of a macroscopic, continuum-based formulation for dissipative functional materials with electro-magneto-mechanical couplings is presented based on incremental variational principles. Phenomenological approaches are applied to model the nonlinear constitutive behaviour of ferroelectric and ferromagnetic phases, and the procedure is applied to determine magnetoelectric coupling properties of a composite with ferroelectric and ferromagnetic particles in an elastic matrix.

In this work, a finite element method (FEM) [28] has been applied for the simulation of spherical, ellipsoidal and fibre-shaped ME structures to investigate the ME effect at the magnetostrictive-electroactive interfaces [19] adapting a method previously reported in Ref. [23]. This operation can be performed either by programing or by any commercially available simulation tool. Polyvinylidene fluoride (PVDF) was selected as the piezoelectric polymer and cobalt ferrite $CoFe_2O_4$ (CFO) as the magnetostrictive counterpart. While PVDF presents an elevated piezoelectric response, large chemical and radiation resistance [29], CFO was selected due to its large magnetostriction, high Curie temperature, and chemical resistance [23,30].

2. Theoretical simulation

2.1. Magnetoelectric model for finite element method simulations

The model is based on both, magnetostrictive and piezoelectric phases being in a stressed state on the bonded interface, such as in Ref. [23].

Briefly, the stressed stated is induced by the presence of an external magnetic field that affects the magnetostrictive phase of the composite. Coupling between the magneto-elastic-electric fields is computed in the two phases, driven by the elastic bonding.

The source of the external magnetic field are Helmholtz coils carrying DC current density (in order to supply a homogeneous magnetic field) and inducing a magnetic-mechanical-electrical coupling that is evaluated in terms of the magnetic vector potential (Ψ), magnetization (M), mechanical displacement vector (u), electric potential (ϕ) and electric polarization (P).

2.1.1. Fundamentals: magnetic field model for magnetostatics

As the current density within the coils (J_e) is a steady current, and according to Maxwell's equation, a magnetic field (H) will be generated, given by Ampere's Law:

$$\nabla \times H = J_e \tag{2}$$

After the Gauss's Law for magnetism, the magnetic flux density, B, is established by:

$$\nabla \cdot B = 0, \text{ implying } B = \nabla \times \psi \tag{3}$$

With Ψ representing the magnetic vector potential, and $\nabla\cdot$ and $\nabla\times$, the mathematical divergence and rotor operators, respectively.

Within the magnetostrictive phase, the magnetic induction (B) can be referred in terms of the applied magnetic field (H) and the magnetization (M). Because the magnetostrictive strains and magnetic permeability within the magnetostrictive phases are nonlinearly influencing the magnetic flux density and strain as stresses, this relation is better represented by Ref. [31]: