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Optimization of the Magnetoelectric Response of Poly(vinylidene fluoride)/Epoxy/Vitrovac Laminates

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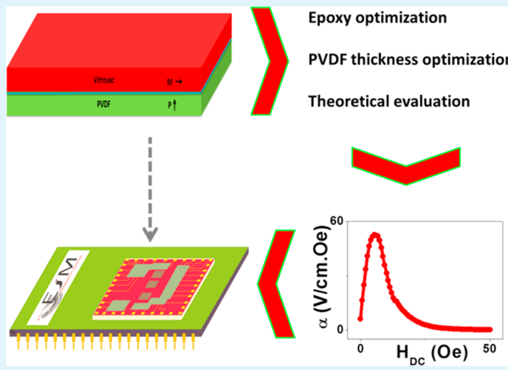
ABSTRACT: The effect of the bonding layer type and piezoelectric layer thickness on the magnetoelectric (ME) response of layered poly(vinylidene fluoride) (PVDF)/epoxy/Vitrovac composites is reported. Three distinct epoxy types were tested, commercially known as M-Bond, Devcon, and Stycast. The main differences among them are their different mechanical characteristics, in particular the value of the Young modulus, and the coupling with the polymer and Vitrovac ($Fe_{39}Ni_{39}Mo_4Si_6B_{12}$) layers of the laminate. The laminated composites prepared with M-Bond epoxy exhibit the highest ME coupling. Experimental results also show that the ME response increases with increasing PVDF thickness, the highest ME response of 53 V·cm^{-1}·Oe^{-1} being obtained for a 110 μm thick PVDF/M-Bond epoxy/Vitrovac laminate. The behavior of the ME laminates with increasing temperatures up to 90 °C shows a decrease of more than 80% in the ME response of the laminate, explained by the deteriorated coupling between the different layers. A two-dimensional numerical model of the ME laminate composite based on the finite element method was used to evaluate the experimental results. A comparison between numerical and experimental data allows us to select the appropriate epoxy and to optimize the piezoelectric PVDF layer width to maximize the induced magnetoelectric voltage. The obtained results show the critical role of the bonding layer and piezoelectric layer thickness in the ME performance of laminate composites.



KEYWORDS: *magnetoelectric, piezoelectric, polymer composites, interface, multiferroic*

1. INTRODUCTION

Magnetoelectric (ME) materials are being increasingly investigated[1] due to their potential applications as sensors, actuators, energy harvesting devices, memories, transformers, filters, resonators, and phase shifters, among others.[1−4]

The main characteristic of ME materials is the variation of the electrical polarization (P) in the presence of an applied magnetic field (H)

$$\Delta P = \alpha \Delta H \quad (1)$$

and the variation of the induced magnetization (M) in the presence of an applied electrical field (E)

$$\Delta M = \alpha \Delta E \quad (2)$$

where α is the *ME* coupling coefficient.[3,5−7]In this way, through the ME effect the cross-correlation between the magnetic and the electric orders of matter can be achieved.

In multiferroic (MF) single-phase materials this effect is intrinsic and attributed to the coupling of magnetic moments and electric dipoles.[3,5,6] Nevertheless, single-phase ME materials, so far, exhibit low Curie temperatures and show weak ME coupling at room temperature, hindering in this way their incorporation in technological applications.[7,8]

In multiple-phase ME materials this effect is extrinsic, emerging in an indirect form, through an elastic-mediated coupling between a piezoelectric phase and a magnetostrictive phase.[2,3,9]

Three main types of nonpolymer-based ME composites are found in the literature:[2,3] (i) particulate composites of ferrites and piezoelectric ceramics (e.g., lead zirconate titanate (PZT));[7,10−12] (ii) laminate composites of ferrites and piezoelectric ceramics;[12−14] and (iii) laminate composites of magnetostrictive metals/alloys (e.g., Terfenol-D or Metglas) and piezoelectric ceramics.[15−18] The above-mentioned composites are thus based on piezoelectric ceramics, which are therefore dense and brittle and can lead to fatigue and failure during operation. Moreover, those materials have low electrical resistivity and high dielectric losses which can hinder specific applications.[19,20] The use of piezoelectric polymers, such as poly(vinylidene fluoride), PVDF, and its copolymers can solve some of the problems found in ceramic composites since they are flexible, show large electrical resistivity and small losses, and

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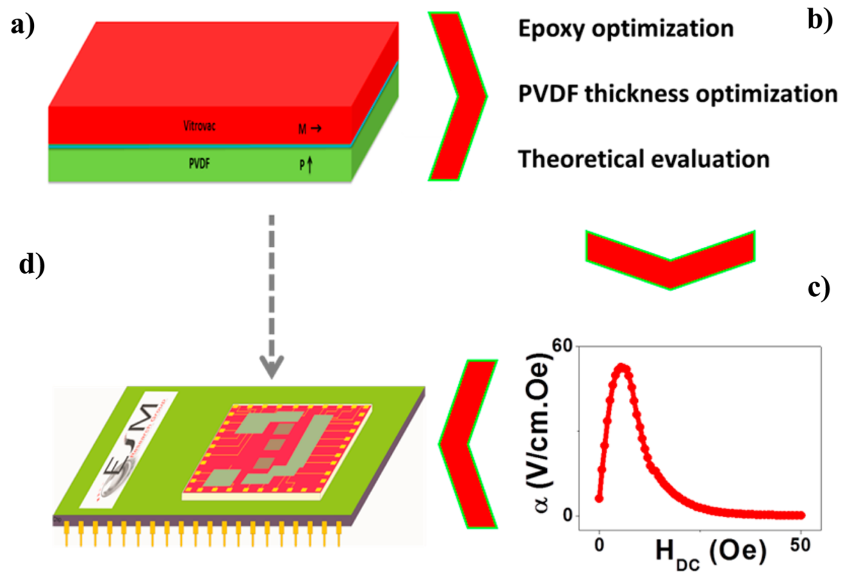

Figure 1. Schematic representation of the Vitrovac/epoxy/PVDF composite (a), the optimization process (b), and its ME response (c) which pave the way for its incorporation into technological applications such as magnetic sensors (d).

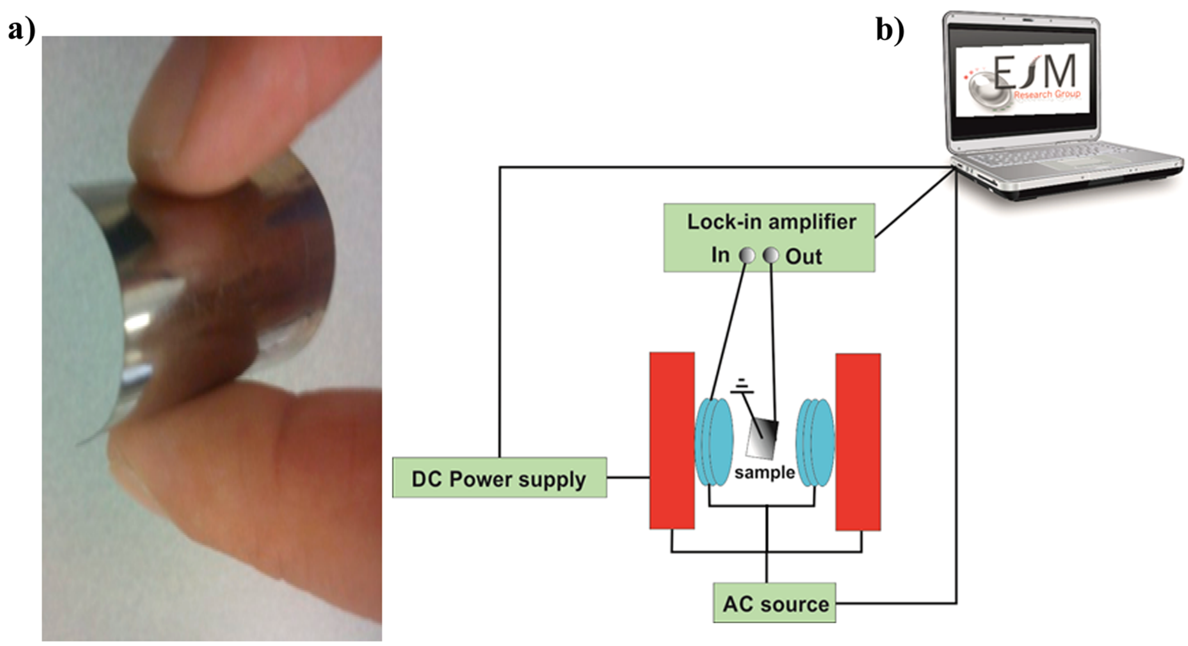

Figure 2. (a) Flexible ME material and (b) representation of the ME measurement setup.

can be easily fabricated by large- and small-scale low-temperature processing methods into a variety of forms.[20−23]

Regarding polymer-based ME materials, three main types of composites can be found in the literature: (i) nanocomposites, (ii) polymer "as a binder", and (iii) laminated composites.[4] Laminated polymer-based ME materials are those with the highest ME response. In particular, Fang et al.[24] reported a magnetoelectric voltage coefficient of 21.46 V·cm^{-1}·Oe^{-1} for a laminate comprising PVDF, Metglas 2605SA1, and Devcon epoxy. Such a value was achieved at non-resonance frequencies by taking advantage of the flux concentration effect[25] and is, so far, the highest response among this kind of materials at non-resonance frequencies. At the longitudinal electromechanical resonance, Jin et al.[26] reported a magnetoelectric voltage coefficient of 383 V·cm^{-1}·Oe^{-1} on cross-linked P(VDF-TrFE)/Metglas 2605SA1 bonded with an epoxy resin, the highest value reported to date.

Despite those high values of ME response on polymer-based ME laminates, proper description, characterization, and optimization of both piezoelectric and magnetostrictive phases, the optimization of the element responsible for the coupling between the phases (usually an epoxy) remains poorly studied.[27,28]

Trying to solve this limitation, in this work, PVDF was bonded to Vitrovac ($Fe_{39}Ni_{39}Mo_4Si_6B_{12}$) with three epoxies with different elastic moduli to study their effect on the ME response.

Vitrovac 4040 was used as the magnetostrictive component not for its magnetostriction value (λ = 8 ppm), actually modest, but for its high piezomagnetic coefficient (1.3 ppm/Oe) at low

Table 1. Material Properties of the Piezoelectric PVDF Polymer[39,40]

property	value
density, ρ	1780 kg/m^3
elasticity matrix, $\mathbf{c}_E$ (Pa)	(xx, yy, zz, yz, xz, xy) {{2.74 × 10^{09}, 5.21 × 10^{09}, 4.78 × 10^{09}, 0, 0, 0}, {5.21 × 10^{09}, 2.36 × 10^{09}, 5.21 × 10^{09}, 0, 0, 0}, {4.78 × 10^{09}, 5.21 × 10^{09}, 2.12 × 10^{09}, 0, 0, 0}, {0, 0, 0, 2.74 × 10^{09}, 0, 0}, {0, 0, 0, 0, 2.74 × 10^{09}, 0}, {0, 0, 0, 0, 0, 2.74 × 10^{09}}}
compliance matrix, $\mathbf{c}_E^{-1}$ (Pa^{-1})	(xx, yy, zz, yz, xz, xy) {3.65 × 10^{-10}, −1.92 × 10^{-10}, 4.24 × 10^{-10}, −2.09 × 10^{-10}, −1.92 × 10^{-10}, 4.72 × 10^{-10}, 0, 0, 0, 3.65 × 10^{-10}, 0, 0, 0, 0, 3.65 × 10^{-10}, 0, 0, 0, 0, 0, 3.65 × 10^{-10}}
coupling matrix, $\mathbf{e}$ (C·m^{-1})	(xx, yy, zz, yz, xz, xy) {{0, 0, −4.761, 0, 0, −33.33}, {0, 0, 3.703, 0, 1.703, 0}, {1.703, 0, 0, 0, 0, 0}}
relative permittivity, ε_S	{{13, 0, 0}, {0, 13, 0}, {0, 0, 13}}

magnetic fields (≈15 Oe) and low cost.[29] PVDF was chosen as the piezoelectric component since it exhibits the highest piezoelectric response among polymers.[22,30]

To numerically evaluate the experimental results, a finite element method (FEM) based simulation was also performed. To date, a wide amount of numerical approaches have been used to determine the ME response of piezoelectric/magnetostrictive composites, namely, the Green's function technique,[31−33] the finite element method,[28,34] the constitutive equations,[35] the numerical statistical analysis,[36] and the effective medium approximation.[37] Nevertheless, considering that both magnetostrictive and piezoelectric behaviors are anisotropic, and taking into account that in the ME structure reported in this work both layers are separated by an epoxy bonding layer that incorporates specific mechanical coupling factors into the final ME response, the approach that best fits the evaluation of the macroscopic experimental response is the FEM.

In this way, the ME response of the ME structure was studied as a function of the PVDF thickness, and the epoxy properties and the results were numerically evaluated with the final goal to optimize such materials for applications in innovative technological applications such as magnetic sensors (Figure 1).

2. EXPERIMENTAL SECTION

Commercial poled β-PVDF films with thicknesses of 28, 52, and 110 μm with Cu−Ni electrodes deposited on both sides were purchased from Measurement Specialties, USA, and used as provided (d_{33} = −33 × 10 and d_{31} = 23 × 10 pC/N). All PVDF samples were cut into rectangular shapes with 50 mm × 10 mm size using a clean and sharp scalpel. The PVDF piezoelectric response (d_{33}) was verified with a wide range d_{33}-meter (model 8000, APC Int. Ltd.) to ensure that the cutting process had no effect on the piezoelectric response of the polymer.

Vitrovac 4040 ($Fe_{39}Ni_{39}Mo_4Si_6B_{12}$) and 30 mm × 6 mm × 25 μm magnetostrictive ribbons were used as magnetostrictive components. All ME laminates were fabricated as represented in Figure 1a. An image of the ME laminate is shown in Figure 2a.

To study the effect of each epoxy on the ME response, laminated composites were prepared by gluing the piezoelectric layer to the magnetostrictive layer with three different epoxy resins, chosen due to their distinct mechanical properties (Young Modulus given in the brackets): ITW Devcon 5 minute Epoxy (0.7 GPa), Strain Gage Adhesive M-Bond 600 - Vishay Precision Group (0.3 GPa), and Stycast 2850 FT blue (9 GPa). The Young modulus of the epoxy resins was determined from the initial slope of strain−stress curves measured using a Shimadzu AG-IS universal testing machine in tensile mode, with a 2 mm min^{-1} loading rate (data not shown).

ME measurements were performed simultaneously applying an H_{DC} magnetic field ranging from 0 to 50 Oe and a superimposed H_{AC} field equal to 0.13 Oe at resonance frequencies ranging from 30 to 45 kHz. The ME response of the laminate was determined as

$$\alpha_{ME} = \frac{dE}{dH} = \frac{1}{t}\left(\frac{\delta V}{\delta H_{AC}}\right) \tag{3}$$

where δH_{AC} is the applied AC magnetic field amplitude; δV is the induced magnetoelectric voltage; and t is the thickness of the piezoelectric polymer. The measurement of δV was performed with an SR830 DSP lock-in amplifier.

Temperature-dependent magnetoelectric-induced voltage between room temperature and 85 °C was performed by introducing the whole experimental setup (sample, exciting, detecting, and bias coils) inside a climatic chamber. Each sample was tested at conditions of resonant frequency and optimized DC field, to obtain the maximum ME response.

3. NUMERICAL MODEL BY THE FINITE ELEMENT METHOD

Assuming the linear range of magnetostriction, the electromechanical coupling of the three-layer (piezoelectric + epoxy + magnetostrictive) ME structure (Figure 1a) was modeled by the finite element method (FEM) to obtain the numerical ME response. A 2D approximation has been considered by establishing the ME response to be constant along the width of the structure. The model additionally considers the ME structure as composed by three flexible films—magnetostrictive layer of Vitrovac, epoxy layer, and piezoelectric layer of PVDF—properly glued to each other with an appropriate coupling between the structural and electrical fields. This coupling is fulfilled by the continuity equations on the stationary case, given by

$$\nabla \cdot D = \rho_v \quad \text{(Gauss Law, } t = 0) \tag{4}$$

$$\nabla \cdot \sigma = f_v \quad \text{(Cauchy Momentum Equation, } t = 0) \tag{5}$$

Here "∇·" represents the divergence, D the electrical displacement field, ρ_v the free electric charge density, σ the stress tensor, and f_v the force per unit volume.

The constitutive equations for the fully coupled piezoelectric material consist of the direct and indirect piezoelectric effects and are given by[38]

$$\mathbf{T} = \mathbf{c_E S} - \mathbf{e^T E} \tag{6}$$

$$\mathbf{D}_A = \mathbf{e_S S} + \varepsilon_\mathbf{S} \mathbf{E} \tag{7}$$

where $\mathbf{T}$ is the mechanical stress matrix, $\mathbf{S}$ the mechanical strain matrix, $\mathbf{E}$ the electric field vector, and $\mathbf{D}_A$ the electric charge vector per unit area.

A coupling coefficient (k) was included to represent the mechanical coupling between the epoxy and both Vitrovac and PVDF layers. Such a coefficient was set to be between 0 (not coupled) and 1 (ideal coupling).

The input parameter for the calculations will be $\mathbf{S} = \lambda(H)$, which is the magnetically induced magnetostrictive strain in the Vitrovac 4040 constituent.

The material properties of the poled piezoelectric PVDF polymer are described by the mechanical stiffness matrix at constant electric field $\mathbf{c}_E$, the permittivity matrix under constant strain ε_S, and the piezoelectric stress matrix $\mathbf{e}_S$. These properties are shown in Table 1.

The three layers forming the ME structure are represented in Figure 1a together with the polarization and magnetization directions. The size of the ME structure was set to be 30 mm × 10 mm. The thickness of the magnetostrictive layer was fixed to 25 μm, and its mechanical properties are shown in Table 2. The experimental cases of piezoelectric layer thickness of 28, 52, and 110 μm are studied taking a constant epoxy thickness of 12 μm (determined by scanning electron microscopy (SEM)).

Table 2. Mechanical Properties of Vitrovac 4040

property	value	unit
density (ρ)	7900	kg/m^3
Poisson's ratio (ν)	0.27	-
Young's modulus (Y)	1500	MPa

The numerical evaluation consisted of applying a deformation on the two lateral ends of the magnetostrictive layer consistent with the magnetostrictive response of the material[41,42] and evaluating the electrical potential obtained across the piezoelectric layer. The applied deformation of the magnetostrictive Vitrovac 4040 will be obtained from the magnetic field–magnetostriction curve of the material.[41] It will be chosen in all cases as the strain corresponding to the maximum deformation experienced by the magnetostrictive layer. Structurally, when the three layers are perfectly bonded, the deformation on the magnetostrictive layer will produce a deformation on the other two layers, which will depend on their mechanical properties. The electrical ground was set at the outer surface of the piezoelectric layer, locating also a compliant electrode between the piezoelectric and the bonding layer. The ME structure is set to deform only along the longitudinal direction.

The influence of the bonding layer Young modulus on the ME performance of the structure was thus simulated together with the ME response of the laminate by varying piezoelectric and bonding layer thickness, to optimize the ME response of the fabricated multilayer structures.

3. RESULTS AND DISCUSSION

Figure 3 shows the ME response of laminate composites of 110 μm thick PVDF films bonded with Devcon, M-Bond, and Stycast to Vitrovac magnetostrictive substrates.

The obtained results reveal the strong influence of the epoxy layer on the ME response of the composite.

The highest ME response has been obtained for the M-Bond bonded composites, the epoxy with the lowest Young modulus; on the contrary, the lowest response is obtained for Stycast bond end composites, which is the epoxy with the highest Young modulus and lower k value used.[27,28,43] It is observed that with higher Young modulus the epoxy loses its ability to transmit the deformation from the magnetostrictive layer to the piezoelectric layer due to the increased rigidity, leading to a decrease in the coupling factor from 0.6 to 0.07, revealing an interface detachment between the active layers (magnetostrictive and piezoelectric) and the epoxy layer. Further, the highest ME response is obtained at the lowest applied H_{DC} field by using the M-Bond; in correspondence, Stycast shows the lowest ME response at the highest applied H_{DC} field. Devcon-containing composites show an intermediate behavior. This relationship between the ME response and the Young modulus shows the relevance of the latter parameter for the fabrication of devices and indicates the best choice for ME performance optimization. These results are supported by the simulations as the images obtained by FEM (Figure 3c, d, and e). Red colors indicate the minimum potential, and the blue colors indicate the maximum potential in the static analysis.

As the M-Bond bonded laminates show the highest ME response, this epoxy was used in the study of the effect of the thickness of the PVDF layer on the ME response of PVDF/M-Bond/Vitrovac laminates.

PVDF layers with 28, 52, and 110 μm were used, and the effect of the piezoelectric layer thicknesses on the ME response of the composites was evaluated, both experimentally and through numerical FEM simulations. Figure 4a shows the magnetoelectric coefficient as a function of the DC applied field and Figure 4b the comparison of experimentally and numerically obtained values of the ME coefficient for the different piezoelectric layer thicknesses.

As previously reported, Figure 4 shows that the ME response of PVDF-based ME-laminated composites increases with increasing thickness of the PVDF layer.[44] Nevertheless, an increase of 300% in the thickness of PVDF (from 28 to 110 μm) has, as a consequence, just an increase of 20% in the ME response (from 45 to 53 V·cm^{-1}·Oe^{-1}).

In the images obtained by the FEM simulations (Figure 4c, d, and e), it can be observed that the intensity of the red and blue colors increases with increasing thickness of PVDF. With increasing the PVDF layer thickness, a larger number of dielectric moments suffer variation under the applied stress, resulting in a higher ME response.[43] However, it should be noted that a maximum value must exist for the PVDF thickness at which the ME response is maximized as a larger thickness will lead to inhomogeneous deformations of the material, with more deformation at the boundary layer with the binder and lower deformation at the down side, thus decreasing its ME response,[43] as shown in the simulation represented in Figure 5.

Figure 5 shows that for a very thick layer of PVDF (750 μm) the deformation generated by Vitrovac is only transmitted to a volume fraction of the PVDF layer close to the epoxy layer,

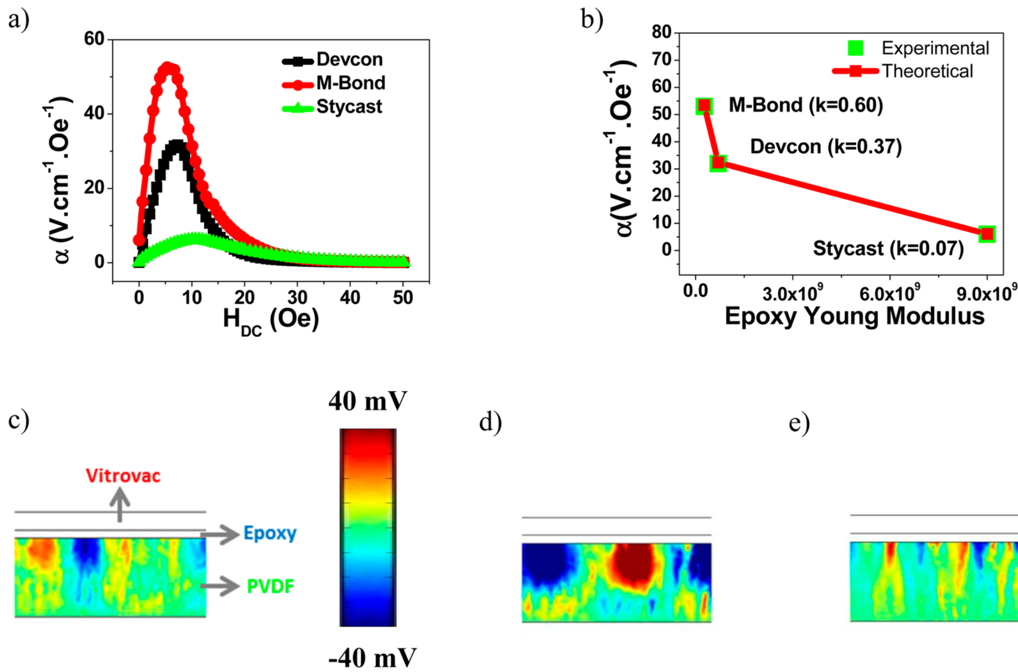

Figure 3. (a) Magnetoelectric response, α, at resonance obtained for the PVDF/epoxy/Vitrovac composites for a 110 μm PVDF layer and different epoxy binders. (b) Relation between α and the epoxy Young modulus. Images from the numerical simulation of the ME effect in laminates bonded with: (c) Devcon; (d) M-Bond, and (e) Stycast. Part c also shows the color scale of the FEM simulations.

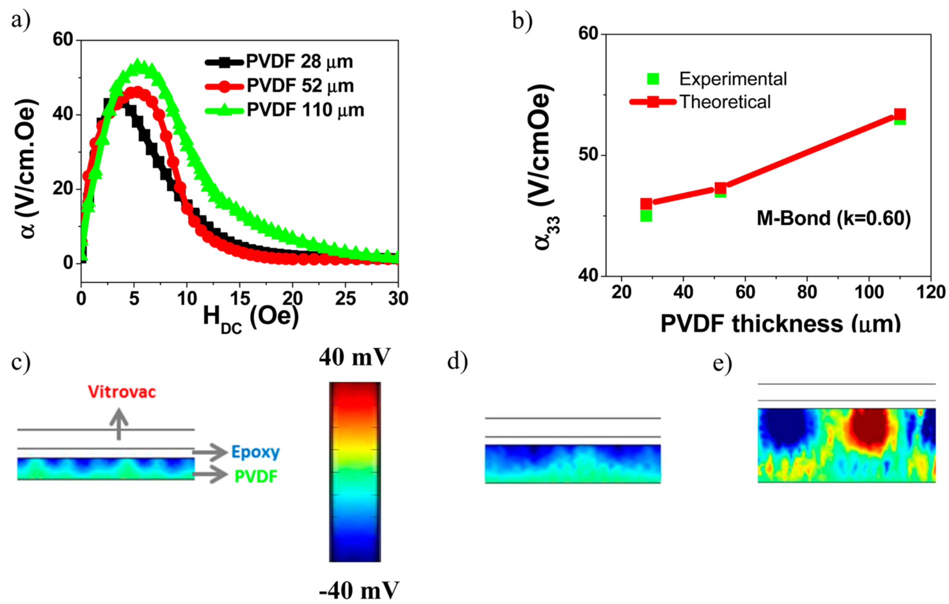

Figure 4. (a) Magnetoelectric coefficient, α, measured at the resonance frequency as a function of the DC magnetic field for the piezoelectric layer of different thickness and (b) comparison between the experimental and numerical results. Images from the FEM simulation of the ME effect in laminates bonded with M-Bond epoxy with PVDF thickness of: (c) 28 μm; (d) 52 μm; and (e) 110 μm. Part c also shows the color scale of the FEM simulations.

causing the observed decrease of the magnitude of the ME effect.

Another important parameter for practical applications is the thermal stability of the device. Figure 6 shows the variation of the ME response with temperature in the temperature range 20−85 °C for a PVDF 110 μm/M-Bond/Vitrovac laminate. The maximum temperature of 85 °C was chosen, as around that temperature PVDF undergoes the α-relaxation leading to strong shrinking of the material.[45]

As previously reported,[29] the ME response of PVDF-based materials decreases with increasing temperature. This decrease is not mainly explained by the depoling effects (related to increased molecular mobility with increasing temperature) which leads to a decreased piezoelectric response since just a decrease of 20% in the PVDF piezoelectric coefficient is reported when the temperature increases until 100 °C.[46] Figure 6 demonstrates a decrease of more than 80% in the ME response of the laminate which is related with a decrease of the coupling, defined as k, between the epoxy and the active layers

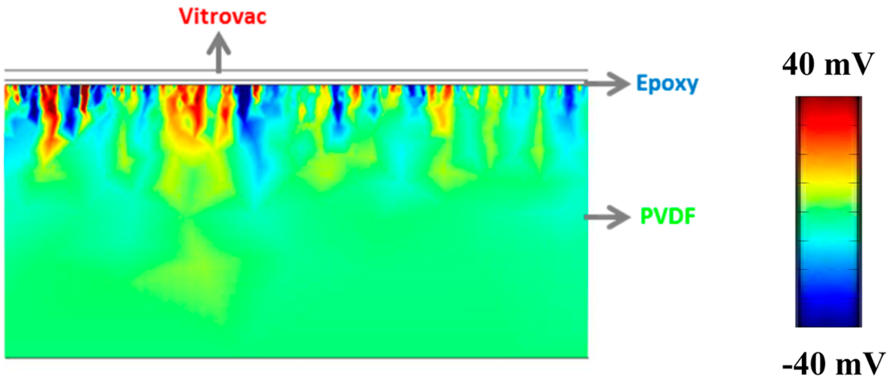

Figure 5. Numerical simulation of a thick PVDF layer (750 μm) bonded to a Vitrovac layer with M-Bond epoxy (12 μm). The corresponding color scale is shown on the right.

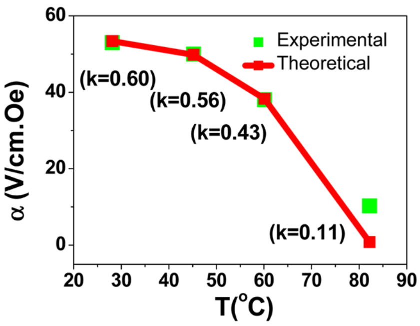

Figure 6. Temperature dependence of the magnetoelectric coefficient, α, measured at the resonance frequency for the composites PVDF (110 μm)/M-Bond/Vitrovac.

of the laminate. The coupling factor k varies from 0.6 at room temperature to 0.11 at 80 °C and reflects a weaker coupling between the layers due to a softening of the materials leading to a smaller k. The results in Figure 2 suggest that softer materials possess higher k value. In this way, the k value decrease revealed in Figure 5 should be related with the temperature-dependent deformations that lead to interface detachment (due to the different thermal expansion coefficients of the material) and therefore reduced transduction capability.

Despite the temperature effect on the ME response, the ME coupling coefficient still remains at suitable values up to temperatures of 80 °C, which allows widespread use for sensor and actuator applications. In a similar way, it has been reported that PVDF still retains stable piezoelectric response after temperature annealing at 140 °C, with a value of ∼−4 pC/N, which is still high for polymer systems,[46] making this polymer an appropriate choice for the development of the flexible, low cost, and easy shaping ME materials with large potential for device fabrication.[4]

Finally, the ME response of the laminates was numerically optimized regarding the epoxy properties (Young Modulus and thickness) and the thickness of the PVDF piezoelectric layer (Figure 7).

Figure 7a reveals that at the 10^6 Pa Young modulus value an abrupt change in the epoxy behavior occurs. For lower values the epoxy behaves as a rubber, stretching in the vicinity of the magnetostrictive material and cringing in the vicinity of the PVDF layer. For higher values of the Young modulus, the epoxy loses its ability to transmit the deformation from the magnetostrictive layer to the piezoelectric layer due to the increased rigidity, having as a consequence a decrease in the ME response.

Increasing the epoxy thickness leads to an increase of the ME voltage coefficient explained by a better coupling between the epoxy layer and the other two layers, as represented in Figure 7b. From a certain value of epoxy thickness, the glue loses the ability to transmit the deformation between the layers, the decrease being explained by the high distance between the layer in which the deformation occurs (Vitrovac) and the layer on which the deformation has to be transmitted (PVDF). As a consequence, part of the deformation is damped along the thick epoxy layer. Thicker epoxy layers will also limit the ME response due to low mechanical strength and contribute toward increasing noise level and aging.[47]

Figure 7c shows an increased ME as a response to the increase of the PVDF layer thickness until it reaches the value of 700 μm.

As previously mentioned, increasing the PVDF layer thickness gives as a first consequence that a larger number of dielectric moments will suffer variation under the applied stress,

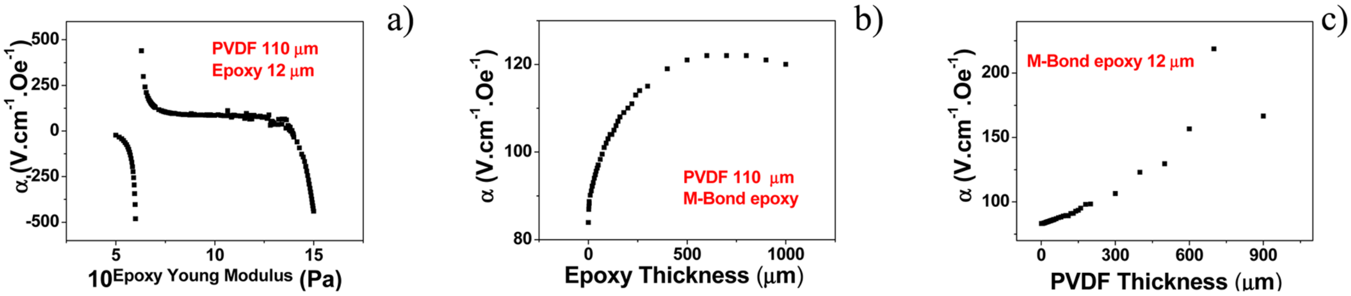

Figure 7. Numerical ME response as a function of (a) epoxy Young modulus, (b) epoxy thickness, and (c) PVDF layer thickness.

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resulting in a higher ME response;[43] nevertheless, above 700 μm thick layers, inhomogeneous deformations of the material will be obtained, with larger deformations at the boundary layer with the binder and lower deformation far from that layer, thus decreasing the ME response.[43]

4. CONCLUSIONS

The effect of the bonding layer type and piezoelectric layer thickness on the ME response of layered poly(vinylidene fluoride) (PVDF)/epoxy/Vitrovac composites is reported. The materials have been experimentally and numerically studied through the FEM model, including the magnetoelastic and piezoelectric laws. An increase of the ME voltage coefficient from 45 to 53 $V\cdot cm^{-1}\cdot Oe^{-1}$ with increasing PVDF thickness from 28 to 110 μm and a reduction of the ME voltage coefficient from 53 to 6 $V\cdot cm^{-1}\cdot Oe^{-1}$ with increasing epoxy Young Modulus from 2.7×10^8 to 9.0×10^9 Pa are verified.

The k value, indicative of the quality of the bonding between the active layers and the epoxy layer, is the highest for the M-Bond laminates (0.60) and lowest for the Stycast laminates (0.07). Stycast laminates exhibit an intermediate behavior. Also regarding the k values, it is found that it decreases with increasing temperature due to interface detachment and leading to reduced transduction.

Good agreement between the FEM model and the experimental results was obtained for PVDF/epoxy/Vitrovac trilayer composites allowing the model to be used for optimizing the epoxy properties (Young modulus and thickness) and the thickness of PVDF to obtain the highest ME coupling on the laminates.

The highest ME response of 53 $V\cdot cm^{-1}\cdot Oe^{-1}$ obtained for a PVDF (100 μm thick)/M-Bond epoxy/Vitrovac laminate as well as the possibility to optimize such value taking into account the Young modulus and thickness of the epoxy and the PVDF thickness make this laminate an excellent candidate to be used in applications such as sensors, actuators, energy harvesting devices, and memories.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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