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Wide-range magnetoelectric response on hybrid polymer composites based on filler type and content

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Abstract: In order to obtain a wide-range magnetoelectric (ME) response on a ME nanocomposite that matches industry requirements, Tb0.3Dy0.7Fe1.92 (Terfenol-D)/$CoFe_2O_4$/P(VDF-TrFE) flexible films were produced by solvent casting technique and their morphologic, piezoelectric, magnetic and magnetoelectric properties investigated.

The obtained composites revealed a high piezoelectric response (≈-18 $pC.N^{-1}$) that is independent of the weight ratio between the fillers. In turn, the magnetic properties of the composites were influenced by the composite composition. It was found that the magnetization saturation values decreased with increasing $CoFe_2O_4$ content (from 18.5 to 13.3 $emu.g^{-1}$) while the magnetization and coercive field values increased (from 3.7 to 5.5 $emu.g^{-1}$ and from 355.7 to 1225.2 Oe, respectively) with increasing $CoFe_2O_4$ content.

Additionally, those films showed a wide-range dual-peak ME response at room temperature with the ME coefficient increasing with weight content of Terfenol-D, from 18.6 $mV.cm^{-1}.Oe^{-1}$ to 42.3 $mV.cm^{-1}.Oe^{-1}$.

Keywords: Magnetoelectric; composite; magnetostrictive; piezoelectric; Wide-range magnetic field

1. Introduction

Magnetic sensors and energy harvesters have attracted much interest in recent years due to their wide range of applications, which include navigation systems, medical sensors, non-destructive material testing, building monitoring, agriculture management and in biomedical areas [1-4], among others.

Traditional magnetic sensors show important disadvantages, which include the need of power supply, low spatial resolution, complex fabrication process, miniaturization problems (for device dimensions on the order of micrometers), high-cost assembly, the need for temperature compensation circuits, large initial offset and reduced accuracy. Furthermore, those devices do not meet increasing industry demands in terms of flexibility, versatility, lightweight, cost, complicated shape allowance or low-temperature fabrication processing, hindering their use in novel and rapidly growing application areas such as flexible or wearable devices [3, 5].

Polymer-based magnetoelectric (ME) materials are attracting increasing attention once they can solve the above-mentioned problems due to their cheap, facile, scalable and low-temperature fabrication methods, the absence of large leakage currents, the ability to fabricate them in a variety of forms—such as thin sheets or molded shapes, and in some cases their biocompatibility[2, 5-8].

ME coefficients on polymer-based ME materials are of the same order of magnitude as the best ones obtained in materials that are already being used/investigated as magnetic sensors and/or energy harvesters. This fact encourages the emergence of a new next generation of polymer-based

ME devices[9-10]. The ME voltage coefficient, as the figure of merit of a magnetic field sensor, describes the variation of the electric field as a function of the applied magnetic field [3]. However, magnetoelectric composites present strong ME effects only near an optimum DC magnetic field, where the effective piezomagnetic coefficient of the magnetostrictive layer is maximum, being this fact the main disadvantage of magnetoelectric devices, as it compromises their use in high-sensitivity miniaturized magnetic devices[3].

Trying to solve such limitation some efforts have been devoted to obtain a multi-peak ME phenomenon on ME devices such as the one proposed by *Chen et al*[3]. In such study the interaction between Terfenol-D and FeSiB resulted in dual-peak occurrence, being the first peak caused by the strong exchange coupling effect between Terfenol-D and FeSiB layers and the second peak caused by the maximum of the dynamic piezomagnetic coefficient q_{33} of the Terfenol-D layer. This pioneer report proved that it was possible to tailor and optimize the ME response by combining different magnetostrictive components in the same ME composite. On the other hand, the developed composite was a laminated structure that shows several drawbacks, such as the effective ME coupling of the (2-2) film connectivity being limited by the clamping of the films to the substrate and detrimental dielectric leakage currents[11]. A possible solution will be the use of nanocomposites, which offer advantages such as higher flexibility, simpler fabrication, easy shaping, miniaturization possibilities, and the absence of degradation at the piezoelectric/magnetostrictive interface[12-13].

Thus, it is scientifically and technologically relevant to obtain a multi-peak ME response on ME nanocomposites to match material's properties and responses with the ones suitable for practical applications[3].

In this work, two types of highly magnetostrictive particles Terfenol-D and $CoFe_2O_4$ were added to a poly(vinylidene-trifluoroethylene), (P(VDF-TrFE)), piezoelectric matrix aiming to tailor the ME response of polymer-based composites through the variation of the magnetostrictive filler type and content.

Terfenol-D microparticles were selected once they exhibit the highest room temperature magnetostrictive coefficient (600ppm) among microparticles. $CoFe_2O_4$ nanoparticles were selected due to their highest magnetostriction (≈200 ppm) among ferrite nanoparticles [14-15]. Additionally the optimum DC magnetic field, where the effective piezomagnetic coefficient of the magnetostrictive particles is maximized, is different for the two particle types, allowing in this way a double-peak phenomenon of the ME response of the Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) hybrid composite. P(VDF-TrFE) has been selected as the piezoelectric matrix due to its highest piezoelectric responses among polymer materials over a wide range of temperatures[9, 16].

2. Materials and Methods

2.1. Materials

N,N-Dimethylformamide (DMF, pure grade) was supplied by Fluka and P(VDF-TrFE) was supplied by Solvay Solexis. $CoFe_2O_4$ nanoparticles were purchased from Nanoamor with dimensions between 35-55 nm. Terfenol-D powder with a mean particle size of ≈1 μm was obtained from ETREMA Products, Inc. All chemicals were used as received without further purification.

2.2. Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) composite preparation

The multiferroic composites were prepared following procedures reported on [2, 9, 12]. Briefly, the selected filler content of the magnetostrictive phase (Terfenol-D and $CoFe_2O_4$) was added into DMF solvent and placed in an ultrasound bath for 8 h aiming to ensure a good dispersion of the magnetostrictive phase. P(VDF-TrFE) polymer was then added and mixed for 2 hours with a Teflon mechanical stirrer in an ultrasound bath to prevent magnetic agglomeration during the mixing process. The, the resulting mixture was spread on a clean glass substrate and solvent evaporation and polymer melting were performed inside an oven for 10 minutes at 210 ºC. P(VDF-TrFE) crystallization was achieved by cooling down the composite films to room temperature (≈25 ºC). At the end of the process, the ≈50 μm thick films were peeled from the glass substrate. Flexible ME

composite films were prepared with 40% weigh content (wt.%) of magnetostrictive filler. It has been shown that for such filler content, the films can be poled without electric breakdown and good ME coupling and flexibility are obtained [12]. To study the influence of each magnetostrictive particle type on the ME response of the developed Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) nanocomposites, 3 distinct samples were produced (further refereed in the paper by the name provided in parenthesis): hybrid composites with 10 wt.% (0.02 in volume fraction)of Terfenol-D and 30 wt.% (0.13 in volume fraction) of $CoFe_2O_4$ (10TD/30CFO); 20 wt.% (0.05 in volume fraction) of Terfenol-D and 20 wt.% (0.08 in volume fraction) of $CoFe_2O_4$ (20TD/20CFO); and 30 wt.% (0.08 in volume fraction) of Terfenol-D and 10 wt.% (0.04 in volume fraction) of $CoFe_2O_4$:(30TD/10CFO).

2.3. Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) composite characterization

The morphology of the Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) composites was evaluated via scanning electron microscopy (SEM) with a Quanta 650 FEI scanning electron microscope at 10 kV. Before SEM, samples were coated with gold by magnetron sputtering. Further, composition analysis was carried out by energy-dispersive X-ray microanalysis (EDS) from 0 to 13 keV.

In order to optimize the piezoelectric response, poling of the Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) nanocomposites was performed in a home-made chamber, after an optimization procedure, by corona poling at 10 kV during 120 min at 120 °C and cooling down to room temperature under the applied electric field. The piezoelectric response (d_{33}) of the composites was evaluated with a wide range d_{33}-meter (model 8000, APC Int Ltd). Room-temperature magnetic hysteresis loops were measured with a Microsense 2.2 Tesla Vibrating Sample Magnetometer vibrating sample magnetometer (VSM).

The ME coefficient α_{33} was measured with the application of both DC and AC magnetic fields along the direction of the electrical polarization of the composites, i.e., perpendicular to the surface.

The AC driving magnetic field of 1 Oe amplitude at ≈8 kHz (resonance of the Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) composites) was delivered by a pair of Helmholtz coils and the DC field with a maximum value of 0.5 T was applied by an electromagnet.

The resonance frequency (f_r) of the composites was calculated by using equation 1:

$$f_r = \frac{n}{2t}\sqrt{\frac{E_Y}{\rho}} \quad (1)$$

where n, t, E_Y and ϱ are the harmonic mode order, thickness, in-plane Young's modulus and density of the composites, respectively. The produced ME voltage (ΔV) was measured with a Standford Research Lock-in amplifier (SR530). Circular 1.4 mm-diameter gold electrodes were sputtered on the opposite sides of the samples prior to the ME characterization.

The ME coefficient α_{33} was determined through equation 2:

$$\alpha_{33} = \frac{\Delta V}{t \times B_{AC}} \quad (2)$$

where ΔV is the ME voltage generated in the composite, B_{AC} the AC magnetic field and t the thickness of the ME composite.

3. Results and Discussion

After the flexible samples, such as the one represented in the inset of Figure 1a are obtained, SEM images were taken in order to verify the dispersion and distribution of the magnetostrictive particles inside the P(VDF-TrFE) matrix.

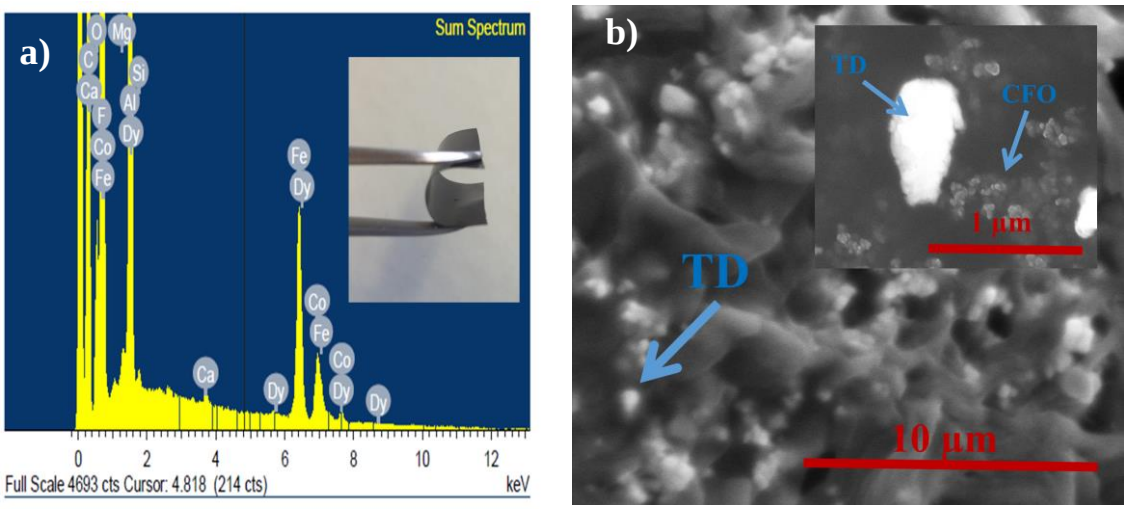

Figure 1. a) EDS analysis of the 20TD/20CFO composite (inset reveals a photograph of such flexible composite); and b) SEM image showing the TD dispersion on the 20TD/20CFO composite as we as a magnification showing both magnetostrictive particles(inset).

Additionally data figure 1a proves the joint presence on the composites of elements of both magnetostrictive particles, Tb, Dy and Fe from TD and Co, Fe and O from CFO.

Figure 1b reveals a good distribution of both particle types inside the polymer. Such good distribution is also observed in the other composite compositions (10TD/30CFO and 30TD/10CFO – images not shown). Additionally, the different size range of TD and CFO fillers is evidenced.

Once the ME response of the TD/CFO/P(VDF-TrFE) composite emerges from the strain-mediated coupling between the piezoelectric and magnetic responses, the effect of filler content and type on these responses was evaluated, as shown in Figure 2.

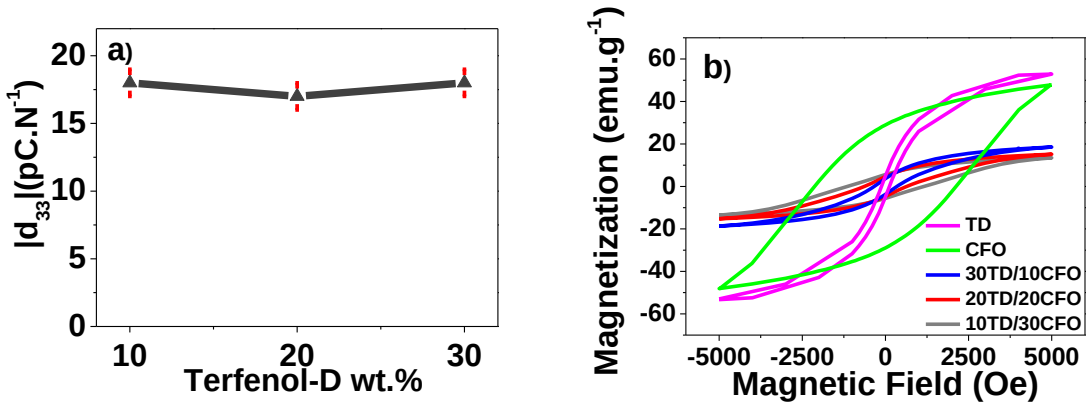

Figure 2. a) Variation of the modulus of the piezoelectric response, $|d_{33}|$ value, as a function of TD/CFO/P(VDF-TrFE) composite composition; b) magnetic response of the TD/CFO/P(VDF-TrFE) composites.

Figure 2a shows that the introduction of magnetic fillers on the polymer matrix leads to a small decrease in the piezoelectric response (≤20%: 18 $pC.N^{-1}$) when compared to the piezoelectric response of neat P(VDF-TrFE) (-22 $pC.N^{-1}$). This fact is attributed to the disruption of the polymer matrix, in particular at the interfaces with fillers. Nevertheless, such piezoelectric response is still suitable for obtaining high ME coefficients on polymer nanocomposites.

Magnetic measurements at room temperature (Figure 2b), allowed to obtain the magnetic behaviour of such composites and compare them with the pure powders (TD and CFO) (Table I).

Table I. Magnetic properties (Magnetization saturation at 5000 Oe: M_S; Remanent magnetization: M_R and Coercive Field: H_C)

Sample	M_S (emu.g^{-1})	M_R(emu.g^{-1})	H_C(Oe)
TD powder	52.9	4.9	117.5
CFO powder	47.8	28.8	2100.3
30TD/10CFO	18.5	3.7	355.7
20TD/20CFO	15.1	4.6	648.1
10TD/30CFO	13.3	5.5	1225.2

It is noted that the M_S value decreases with increasing CFO content (from 18.5 to 13.3 emu.g^{-1}) once CFO powder has lower M_S (47.8 emu.g^{-1}) when compared to TD powder (52.9 emu.g^{-1}). On the contrary, M_R and H_C values increase (from 3.7 to 5.5 emu.g^{-1} and from 355.7 to 1225.2 Oe, respectively) with increasing CFO content, once CFO has higher M_R and H_C values (28.8 emu.g^{-1} and 2100.3 Oe) when compared to TD powder (4.9 emu.g^{-1} and 117.5 Oe). Results from Table I also reveal that the coexistence of both magnetostrictive particles on the same polymeric composite does not hinder the overall magnetic response.

Being proved the appropriate piezoelectric and magnetic responses of the composites, the dependence of the resonant ME voltage coefficient for the TD/CFO/P(VDF-TrFE) composites with the DC bias magnetic field and Terfenol-D content in presented in Figure 3.

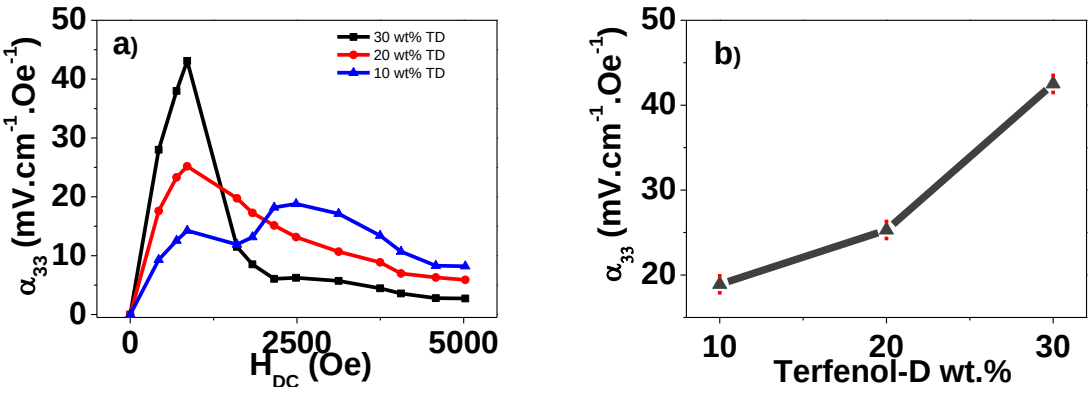

Figure 3. a) ME voltage coefficient (α_{33}) as a function of H_{DC} for the Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) composites; b) variation of the Terfenol-D/$CoFe_2O_4$/P(VDF-TrFE) highest α_{33} value as a function of composite composition.

Due to the magnetostrictive properties of the fillers, the maximum ME response of TD/ P(VDF-TrFE) and CFO/P(VDF-TrFE) hybrid composites usually takes place at 800-1200 Oe and 2000-3000 Oe magnetic field ranges, respectively [17].

In the composite with lower CFO content, 30TD/10CFO, the ME voltage peak is almost entirely derived from the TD magnetostrictive phase, although a smother hump is observable at the 2200-3600 Oe field range.

In the 20TD/20CFO composite, it is verified a ME response with a broad peak as a result of the magnetostrictive properties of both TD and CFO fillers. The 10TD/30CFO composite reveals a double-peak with maximum output voltages at the H_{DC} at which the magnetostrictive coefficient of each nanoparticle type is saturated, 850 Oe and 2500 Oe for TD and CFO, respectively [12].

Due to the higher magnetostrictive coefficient of TD as compared to CFO (600 ppm and 200 ppm, respectively) the composite with higher content of TD particles reaches a higher ME response (Figure 3b) than the one with higher CFO content (30 mV.cm^{-1}.Oe^{-1} and 18 mV.cm^{-1}.Oe^{-1}, respectively).

Such results demonstrate that it is possible to tailor the ME response of the nanocomposites by combining different magnetostrictive fillers in the same composite, allowing the fabrication of high-

sensitivity miniaturized magnetic devices [3]. Additionally, such non single-peak ME response is also useful for energy harvesting devices once it allows a larger energy harvesting performance in a broader magnetic field range.

4. Conclusions

Nanocomposite films based on highly magnetostrictive CFO nanoparticles and TD microparticles dispersed in a piezoelectric P(VDF-TrFE) matrix were prepared by solvent casting with an overall filler content ≈40 wt.%. The obtained multiferroic nanocomposites revealed a stable piezoelectric response (≈-18 $pC.N^{-1}$) that is independent on the weight ratio between the fillers. The magnetization saturation values decrease (from 18.5 to 13.3 $emu.g^{-1}$), whereas the remanent magnetization and coercive field values increase (from 3.7 to 5.5 $emu.g^{-1}$ and from 355.7 to 1225.2 Oe, respectively) with increasing CFO content.

Additionally, these films show a strong ME coupling at room temperature with the ME coefficient increasing with TD content up to 42.3 $mV.cm^{-1}.Oe^{-1}$, for the sample with 30 wt.%. As compared to films with just one magnetostrictive filler, the developed polymer based composite films showed a double-peak wide-range ME response, together with the highest ME response found on polymer-based particulate composites.

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