

Improved magnetodielectric coefficient on polymer based composites through enhanced indirect magnetoelectric coupling

P. Martins^a, D. Silva^a, M. Silva^a and S. Lanceros-Mendez^{a,b,c}

^aCentro/Departamento de Física, Universidade do Minho, 4710-057 Braga, Portugal

^bBCMaterials, Parque Científico y Tecnológico de Bizkaia, 48160-Derio, Spain

^cIKERBASQUE, Basque Foundation for Science, Bilbao, Spain

Particulate composites of ferrite and ferroelectric polymer phases with general formula $[x\text{CoFe}_2\text{O}_4]/[(1-x)\text{PVDF}]$ were prepared for $x = 0, 3, 11$ and 20 wt.% by solution casting.

The dielectric constant, dielectric loss and saturation magnetization of the polymer composite films increase with increasing CoFe_2O_4 (CFO) content, being 13, 0.13 and 13 $\text{emu}\cdot\text{g}^{-1}$ respectively, for $x=20$.

The magnetodielectric (MD) coupling also depend on the CFO content, the change in the dielectric response (MDE(%)) being the highest for the $x=20$ sample (4.2%). On the other hand, the highest value of the MD coefficient (γ) is higher on the $x=3$ sample ($0.015 \text{ emu}^{-2}\text{g}^2$).

Those values are favourably compared with the ones found in the ceramic-based MD materials, being the highest reported for polymer composites.

These facts, together with the flexibility and scalable production of the composites, leads to their large application potential in areas such as filters, magnetic field sensors and actuators, among others.

Keywords: CoFe₂O₄, PVDF, magnetodielectric, nanocomposite, multiferroic

1. Introduction

Actively tuning the dielectric properties of materials is both scientifically relevant and technologically demanded [1]. Among the different ways to achieve this, including the application of driving voltages and magnetic fields, magnetic control of the dielectric response is desirable due to the contactless tuning of the dielectric variation through the application of the magnetic field, providing robust systems with simpler integration into devices [2].

Thus, the magnetodielectric effect (MDE), defined as the variation of the dielectric permittivity as a response to applied magnetic fields, is of increased fundamental and technological interest [3].

Materials exhibiting large MDE are suitable for new devices including tunable filters, four-state memories, magnetic sensors and spin-charge transducers. Thus, many efforts have been dedicated on finding suitable materials with a large MDE [1, 4].

In order to magnetically control the dielectric constant and/or the capacitance on dielectric materials, two main strategies have been used: controlling the interface physics in multilayer systems and amplifying the MDE near (ferro)magnetic transitions in (ferro)magnetic dielectrics [1]. Despite a large increase (over a factor of 100) of the dielectric constant of HgCd_2S_4 has been achieved with a magnetic field of 5 T at 80 K [5], the MDE in single-phase magnetodielectric (MD) materials is typically very weak at room temperature due to material's symmetry restrictions, leading to unsuccessful implementation in technological applications [6, 7].

Thus, one of the most important issues in this field is how to achieve a large MDE near room temperature [8, 9], being composite systems composed by dielectric and magnetic materials [10, 11] the most promising approaches. There are two major mechanisms leading to a large MDE in multiferroic composites: one is the combination of the magnetoresistance (MR) and Maxwell–Wagner effects [12], which is not related to intrinsic magnetodielectric coupling; and the other is the magnetic-field-induced strain-mediated effect through interface coupling [7, 13]. For the first case, the selection of possible materials for the MR-related MDE is significantly broad and, as an example, it has been achieved a room temperature MDE effect of 0.8% under 7 T in core-shell $\text{BaTiO}_3\text{-c-Fe}_2\text{O}_3$ nanoparticles [14]. For the latter case, composites usually consist on a magnetostrictive and a piezoelectric phase

[15]. The applied magnetic field leads to a strain variation in the magnetostrictive component, and the generated stress at the interface induces a dielectric polarization change in the piezoelectric component [16, 17]. Furthermore, this strain can be strongly enhanced near the electromechanical resonance (EMR) frequency [17], which is expected to show a giant MDE response [7]. Following this EMR method, larger MDE can be achieved through material and structure optimization [7].

In this scope, ferrite/piezoelectric ceramic composites, such as $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$, $\text{CoFe}_2\text{O}_4/\text{lead zirconate-titanate (PZT)}$ and Tb–Dy–Fe alloys (Terfenol-D)/PZT, have been found to exhibit room-temperature MD coupling much higher than that of single-phase multiferroics [18]. Additionally, it has been reported that Co@BaTiO_3 core–shell nanotube structures also show significant MD coupling [19]. Traditionally, such ceramic-based composites have been used for designing MD composites but they show several disadvantages, such as high temperature processing, poor flexibility and inability to be designed in a large variety of specific shapes. Thus, polymer-based MD composites arise as an alternative that can solve these issues with advantages also in terms of low processing temperatures and high dielectric breakdown field [20].

In this work, multiferroic composites consisting of magnetostrictive CoFe_2O_4 (CFO) and ferroelectric PVDF have been investigated as possible candidates for high MDE coupling.

This selection relies on the fact that CFO/PVDF composites show high magnetoelectric (ME) coupling for polymer composites [21], thus, the magnetic order is coupled to the polarization and will have an effect on the dielectric constant as well [22]. Since magnetic field affects magnetic ordering, the field will also

indirectly induce variations of the dielectric constant of the magnetoelectric multiferroics [7, 22].

In addition to this expected MDE coupling, such CFO/PVDF composites are particularly interesting due to the proved ability of CFO nanoparticles of inducing the β -phase of PVDF [23], that is the phase with the highest polarity, piezoelectricity and dielectric constant [24].

In this way, a systematic study of the dielectric, magnetic and MD properties of CFO/PVDF polymer composites is presented.

2. Experimental

2.1 Materials and film preparation

All chemicals and particles were used as received from the suppliers: CFO nanoparticles were purchased from Nanoamor with dimensions between 35 and 55 nm. *N,N*-dimethylformamide (DMF, pure grade) was supplied by Fluka and PVDF (Solef 1010) was supplied by Solvay Solexis.

Composites were prepared by using the method reported in [21] for the development of CFO/PVDF ME composites. Briefly, the desired amount of nanoparticles was added to the DMF solvent and the solution was placed in an ultrasound bath for 8 hours for nanoparticle dispersion. Further, the polymer was added and the obtained mixture and

placed in a Teflon mechanical stirrer with ultrasound bath for complete dissolution of the polymer during 2h.

Flexible films were then obtained by spreading the solution on a clean glass substrate and placing them inside an oven at a controlled temperature of ≈ 210 °C for 10 min for solvent evaporation, and cooling down the samples to room temperature for polymer crystallization.. The ferrite nanoparticle content varied from 0 to 20 in weight percent (wt.%), 0 to 0.1 in volume fraction, and the thickness of the samples was ~ 50 μm . Under this conditions, composite samples with good nanofiller dispersion, with PVDF β -phase contents between 80% and 90% and a degree of crystallinity of ≈ 40 % are obtained [23].

2.2 Sample characterization

Measurements of the capacity and $\tan \delta$, dielectric loss, were performed with an automatic Quadtech 1929 Precision LCR meter with an applied voltage of 0.5 V in the frequency range from 1 Hz to 1 MHz. Previously, 5 mm diameter Au contacts were deposited on both sides of the samples with a Polaron SC502 sputter coater, in order to get a plane parallel condenser geometry. The real part of the dielectric constant, ϵ' , was calculated from the capacity measurements taking into account the geometry of the sample.

Magnetic hysteresis loops were measured at room temperature using an ADE 3473-70 Technologies vibrating sample magnetometer (VSM) from -2T to 2T.

In order to obtain the out-of-plane MD coefficient, a *DC* magnetic field was applied by an electromagnet, with a maximum value of 0.5 T, along the perpendicular direction of the electric polarization of the PVDF, i.e., parallel the surface of the composites. The induced change in the dielectric response of the composites was measured with an automatic Quadtech 1929 Precision LCR meter. The MD coupling was studied at

magnetic fields up to 0.5 T, once for higher fields the piezomagnetic coefficient of CoFe_2O_4 decreases, leading to a decrease in the MD response [4].

3. Results and discussion

3.1 Dielectric and magnetic properties

The room temperature variation of the dielectric and magnetic properties as a function filler concentration are shown in Figure 1.

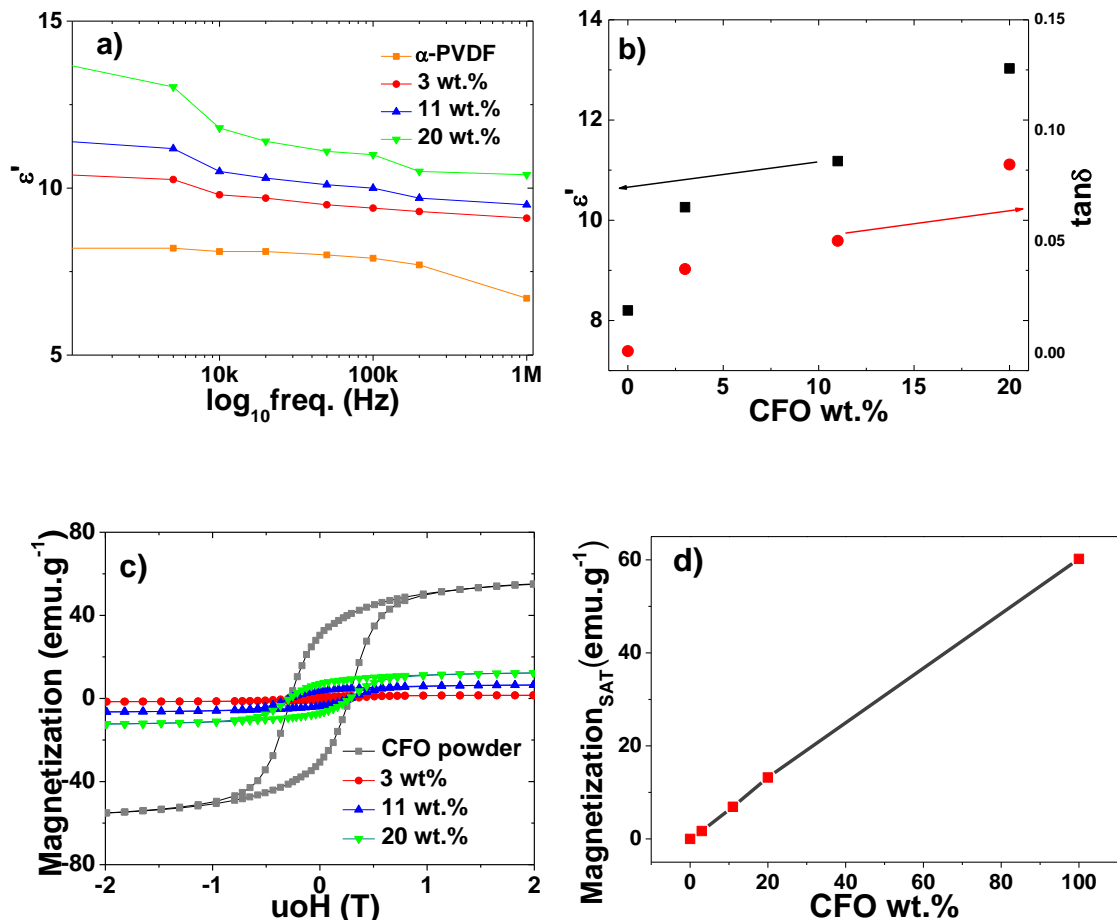


Figure 1. a) Frequency-dependent dielectric constant for CFO/PVDF nanocomposites and; b) variation of the dielectric constant (squares) and dielectric loss ($\tan\delta$ - circles) of the nanocomposites as a function of CFO content at room temperature for a

frequency of 5 kHz; c) Room temperature hysteresis loops for the pure ferrite nanoparticle powder and for the CFO/PVDF nanocomposites. d) Saturation magnetization values as a function of CFO content.

Figure 1a shows that the value of the dielectric permittivity decreases continuously with increasing frequency from 100 Hz to 1 MHz, the decrease being more intense for lower frequencies below 10 kHz. This low frequency response is mostly related to the Maxwell–Wagner contribution at the polymer/nanoparticle interface [25].

Further, the dielectric permittivity increases with increasing filler content from 8 to 13 (at 5 kHz) as CFO increases up to 20 wt%. This increase is accompanied with an increase of the dielectric losses maintaining nevertheless values lower than 0.15 even for the 20 wt% sample. The increase of the dielectric constant with filler content is related both to the increase of the local ionic conductivity and to the nucleation of the β -phase of the polymer which shows a polar nature and higher dielectric constant than the α -phase of PVDF [26].

With respect to the magnetic properties, the shape and magnetization maximum values of the measured hysteresis loops (Figure 1c) reveal the ferromagnetic behaviour of the composites, at room temperature (≈ 300 K) the CFO ferrite behaving as a ferromagnet with blocked magnetic moment within the particles [26]. All composites show a coercive field of ≈ 0.3 T and a saturation magnetization at a 1.5 T applied magnetic field, being the saturation magnetization proportional to the ferrite content within the polymer matrix (Figure 1d) [27, 28].

3.2 Magnetodielectric response

The coexistence of ferromagnetic and dielectric orders allows the coupling between magnetic and electric polarization states and this coupling was measured by monitoring the variation of the dielectric constant with increasing magnetic field (Figure 2).

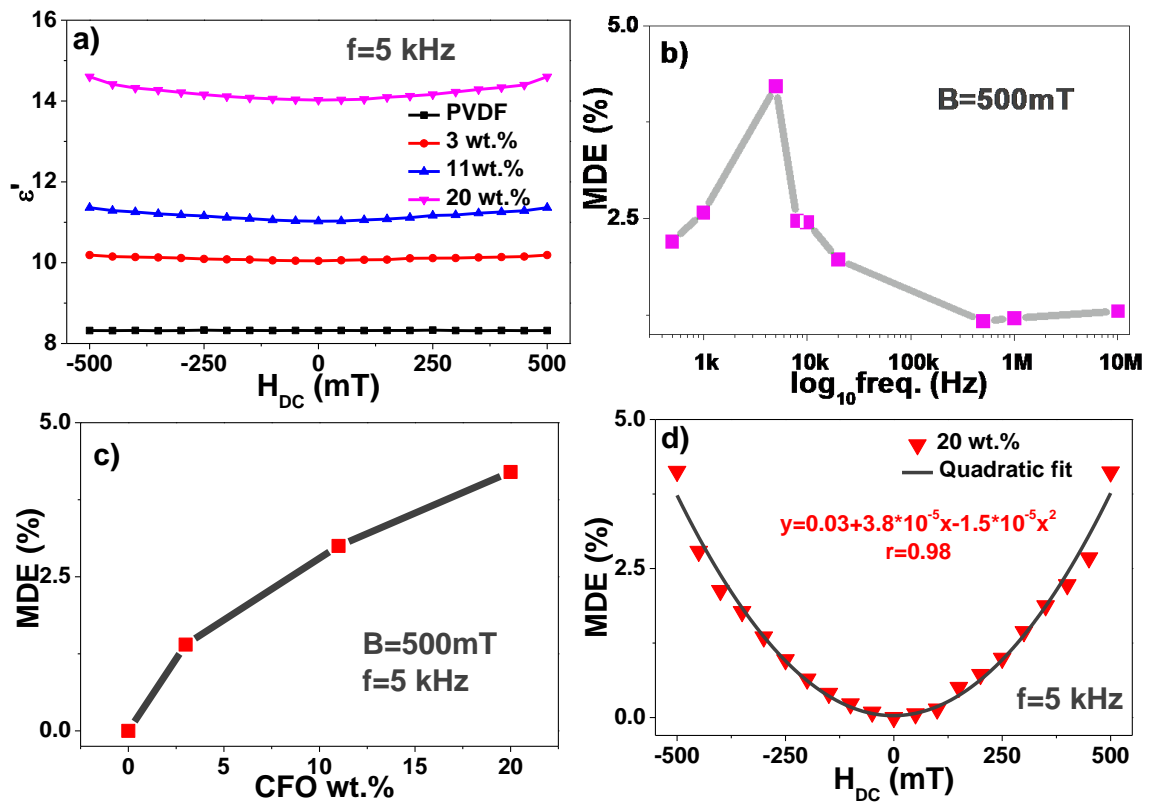


Figure 2. a) Dielectric constant as a function of the DC magnetic field at 5 kHz; b) MDE(%) as a function of the frequency ; c) MDE(%) as a function of the CFO content at 500 mT and 5 kHz; d) Parabolic curve fitting of the MDE(%) as a function of the DC magnetic field.

Figure 2a shows the increase of the dielectric constant with increasing DC magnetic field modulus, being such increase higher for higher filler contents. This variation of the dielectric constant with the applied magnetic field is characterized by the MD constant, defined as $MDE(\%) = (\epsilon_H - \epsilon_0) / \epsilon_0 * 100$, where ϵ_H and ϵ_0 are the dielectric constants with and without the applied magnetic field, respectively [18].

In the present situation, the magnetodielectric coupling occurs due to strain induced (due to the magnetostrictive effect in the nanoparticles) variations of the dipolar order within the polymer, leading to larger dipolar mobility with an applied electric field and, therefore, to an increase the dielectric constant of the composite. Higher DC magnetic fields will generate higher mechanical interaction between PVDF and CFO particles leading to higher MDE (%) [29].

Similar to ME composites, there is an electromechanical resonance frequency at which the MDE is optimized, which is 5 kHz for the CFO/PVDF MD composites (Figure 4b) [17, 27, 28]. The origin of such resonance is related to the acoustic oscillations in the composite, sample geometry and mechanical coupling parameters between nanoparticles and polymer [30-33].

Thus, it is shown that the presence of CFO induces the magnetodielectric coupling of the multiferroic composites, being obtained a MDE(%) of 1.4, 3 and 4.2% for the composites

with CFO contents of 3, 11 and 20 wt.% respectively. Increasing filler content generates higher mechanical interaction between PVDF and CFO particles leading to higher dielectric variations [29], but similar to what happens in ME composites, higher concentrations of CFO nanoparticles leads to losses in the flexibility of the material and increased nanoparticle agglomerates and fragility of the composite [28, 34].

The obtained MDE(%) vs H_{DC} curves (Figure 4d) can be properly fitted with a parabolic equation once the MDE arises from terms proportional to P^2M^2 in a symmetry-allowed Ginzburg–Landau symmetry-allowed Ginzburg–Landau potential to describe the electrical polarization and magnetization, respectively [18]. Such quadratic dependence is observed in many magnetoelectric multiferroic materials [18, 35] where their thermodynamic potential (ϕ) can be written as:

$$\phi = \phi_0 + \alpha P^2 + \frac{\beta}{2} P^4 - PE + \alpha' M^2 + \frac{\beta'}{2} M^4 - MH + \gamma P^2 M^2 \quad (1)$$

where α , β , α' , β' and γ are coupling coefficients. Such ferroelectromagnet material (with coexistence of ferroelectric and ferromagnetic orders) is described by a potential ϕ that can be used to quantify the effect of magnetic ordering on the dielectric susceptibility [4, 36]. The term representing the exchange MD interaction $\gamma P^2 M^2$ is allowed in any ferroelectromagnet as suggested by Kimura *et al.* and Rani *et al.* [36, 37]. In this way, the change of the relative dielectric constant will in turn be proportional to the square of the magnetic order parameter i.e. $\Delta\epsilon \approx \gamma M^2$ (Figure 4).

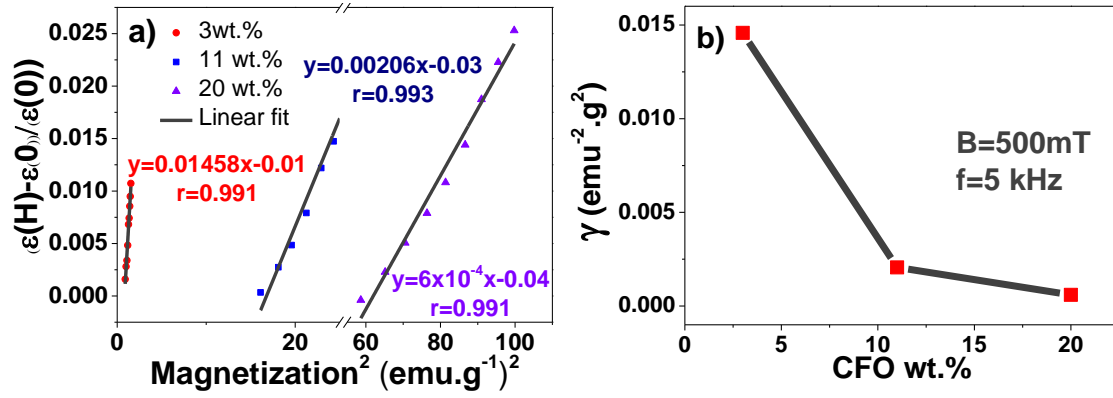


Figure 4. a) Variation of the dielectric constant versus $(M)^2$ plot for the CFO/PVDF composites; b) γ as a function of the CFO content at 500 mT and 5 kHz.

Figure 4a shows that the obtained $(\epsilon(H) - \epsilon(0))/\epsilon(0)$ vs M^2 plots are properly fitted ($r \geq 0.99$), the value of the magnetodielectric interaction coefficient- γ (slope of $(\epsilon(H) - \epsilon(0))/\epsilon(0)$ vs M^2 plots) of the composite samples decreasing from $\approx 0.015 \text{ emu}^{-2}\text{g}^2$ to $6 \times 10^{-4} \text{ emu}^{-2}\text{g}^2$ with increasing CFO content from 3 to 20 wt.%, revealing a lower coupling with increasing filler content. Such decrease in the value of γ with increasing ferrite content has already been reported in other CFO based MD composites [38] and can be related with the increase of dielectric losses and the deterioration of mechanical connectivity with increasing ferrite content due to increasing filler agglomerates.

This decrease in the MD coupling explains the differences between Figure 3c and Figure 4b: the increase of ferrite content in the nanocomposites leads to an increase of the MDE (%) values, but such increase does not take into account the magnetization state of the composite, being necessary to normalize the dielectric response variation to the magnetization variation (γ) in order to properly quantify the MD coupling.

Finally, Table I compares the highest MD coupling parameters (MDE (%) and γ) found in the literature with the one reported in the present study.

Table I. Type of MD material, composition and highest coupling parameters found in the literature.

Materials			Coupling (Temperature, H _{DC})		Ref
Type	Ferroelectric	Magnetic	MDE (%)	γ (emu ⁻² .g ²)	
Single-phase	DyMn ₂ O ₅		100 (3 K, 7 T))	-	[1]
Ceramic Composite	Ba _{1-x} Sr _x TiO ₃	Co _{0.9} Ni _{0.1} Fe _{2-x} Mn _x O ₄	5.3 (300 K, 0.6 T)	-	[39]
Ceramic Composite	Ba _{0.7} Sr _{0.3} TiO ₃	La _{0.67} Sr _{0.33} MnO ₃	7 (300 K, 0.8 T)	4.73	[40]
Ceramic Composite	(Bi _{0.5} Na _{0.5}) _{0.94} Ba _{0.06} TiO ₃	Ni _{0.65} Zn _{0.35} Fe ₂ O ₄	2.19 (300 K, 0.9 T)	5.5x10 ⁻²	[41]
Polymeric Composite	PVDF	Ni	0.03 (300 K, 4 T)	1x10 ⁻¹¹	[18]
Polymer Composite	PVDF	0.8(Bi _{0.5} Na _{0.5})TiO ₃ - 0.2CoFe ₂ O ₄	3.6 (300 K, 0.8 T)	2 x10 ⁻⁶	[36]
Polymer Composite	PVDF	CoFe ₂ O ₄	4.2 (300 K, 0.5 T)	1.5x10 ⁻²	Our

Table I shows that the highest MD coupling is found in single-phase materials, but that this intrinsic MD behaviour is not suitable for technological applications due to the very low temperatures (3 K) and high magnetic fields (7 T).

Further, it is shown that the MDE (%) and γ values obtained in the present work are favourably comparable with the ones found in ceramic-based MD materials. Finally, the

MD coupling reported in the present study is the highest reported for related polymeric composites due to the high ME coupling [16].

Thus, the low value of $\tan\delta$ (≤ 0.15), improved MD effect (4.2% and $1.5 \times 10^{-2} \text{ emu}^{-2} \cdot \text{g}^2$) and flexible nature of the polymer composite films opens the possibility of their use and implementation into devices such as memories, filters, magnetic field sensors and actuators [36].

4. Conclusions

Polymer composites consisting in CoFe_2O_4 nanopowders as ferrite phase and PVDF as ferroelectric phase were prepared by solvent casting. The value of dielectric constant, dielectric loss and saturation magnetization of the polymer composite films increases with increasing CFO content, being maximized for the composite with 20 wt.% of CFO (13, 0.13 and $13 \text{ emu} \cdot \text{g}^{-1}$ respectively).

With respect to the magnetodielectric coupling, increasing filler content from 3 wt.% to 20 wt.% leads to an increase of the MDE(%) values from 1.4 to 4.2% and to a decrease of γ from $0.015 \text{ emu}^{-2} \cdot \text{g}^2$ to $6 \times 10^{-4} \text{ emu}^{-2} \cdot \text{g}^2$, which is related with the increase of dielectric losses and the deterioration of mechanical connectivity with increasing ferrite content due to the appearance of agglomerates.

The obtained elevated MD coupling, the simple processing, flexibility, low weight and ability to be designed in specific shapes, allow these composites to serve as a suitable base for device applications such as tunable filters, magnetic sensors and actuators, among others.

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