



Enhancement of the piezoelectric coefficient in PVDF-TrFe/CoFe₂O₄ nanocomposites through DC magnetic poling

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Abstract

In the last years flexible, low-cost, wearable, and innovative piezoelectric nanomaterials have attracted considerable interest regarding the development of energy harvesters and sensors. Among the piezoelectric materials, special attention has been paid to electroactive polymers such as poly(vinylidene fluoride) (PVDF) and its copolymer poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFe), which is one of the most extensively investigated piezoelectric polymers, due to the high β phase content resulting from specific curing or processing conditions. However, to obtain a high piezoelectric coefficient (d_{33}) alignment of the β phase domains is needed, which is usually reached through applying a high electric field at moderate temperatures. This process, usually referred to as electrical poling, requires the deposition of contact electrodes on the sample surface and the use of high-voltage apparatus. In the present work, in order to overcome these constraints, we have produced, characterized, and studied a polymer nanocomposite consisting of CoFe₂O₄ nanoparticles dispersed in PVDF-TrFe with enhancement of the β phase alignment through an applied DC magnetic field. The magnetic poling was demonstrated to be particularly effective, leading to a piezoelectric coefficient d_{33} with values up to 39 pm/V. This type of poling does not need the use of a top electrode or of high magnetic fields (the maximum value of d_{33} was obtained at 50 mT, using a current of 0.4 A) making the PVDF-TrFe/CoFe₂O₄ nanocomposite suitable for the fabrication of highly efficient devices for energy harvesting and wearable sensors.

Introduction

In the last years, innovative energy harvesting systems based on the piezoelectric effect, able to convert vibrational mechanical energy, which is one of the most present accessible and alternative form of energy, into electric energy, have attracted the interest of the scientific community. The most common piezoelectric materials are ceramics, such as barium titanate, lead zirconate titanate, and lithium niobate, which have a high piezoelectric constant and, therefore, a high conversion efficiency. However, these materials are toxic, brittle, and not environmentally friendly. In order to overcome these disadvantages, several studies have investigated polymeric piezoelectric materials and nanostructured materials with high dielectric constant and good piezoelectric properties suitable for the fabrication of flexible piezoelectric nanogenerators [1-7].

One of the most extensively investigated piezoelectric polymers is poly(vinylidene fluoride) (PVDF). This polymer has attracted a lot of interest due to its excellent piezoelectric and ferroelectric properties, high chemical resistance, high thermal stability, large polarization, short switching time, and mechanical flexibility. All these combined characteristics make it suitable for a wide range of advanced applications, from sensing to energy harvesting [8-11].

It is well known that PVDF is characterized by four main polymorph phases, namely α , β , γ , and δ [12]. Due to its high thermodynamic stability at room temperature the α phase is the predominant one. However, the α phase does not contribute to the piezoelectricity of the polymer, whereas the γ and δ phases, the so-called TGTG' (trans-gauche-trans-gauche) chain conformation, show a weak piezoelectric response after electric poling. The β phase, the so-called TTT (all trans) planar zigzag chain conformation, is the one responsible for the electroactive response of the polymer. It is a polar phase that shows the strongest ferro-, piezo-, and pyroelectric behavior [13], due to the largest spontaneous polarization (7×10^{-30} C·m) [14]. In order to obtain a high content of the β phase, PVDF is generally polymerized with trifluoroethylene (TrFe), producing a copolymer of PVDF, namely poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) [15-17]. This copolymer shows a higher piezoelectric coefficient than PVDF, while still maintaining a high flexibility, sensitivity, and mechanical durability. It is also, like PVDF, a biocompatible polymer.

In order to obtain the best piezoelectric response, the dipoles in PVDF/PVDF-TrFe must be oriented along a preferential direction. The dipole orientation is generally obtained by electrical poling, that is, the application of a strong DC electric field (ca. 10^6 V·cm⁻¹) at elevated temperature (ca. 120 °C) through top and bottom electrodes [18]. However, this technique is not cost-

effective and is not easy in the practical implementation, since it requires the use of high-voltage apparatus. Recently, alternative techniques with respect to electric poling and different strategies have been investigated in order to enhance the β phase content in PVDF. These included mechanical stretching [19,20], spin coating [21], quenching [22], a combination of the latter two techniques [2], and the addition of external additives to the PVDF matrix, such as metal nanocomposites [14,23], ceramic filler [24], and graphene nanoplatelets (GNPs) and their combination with zinc oxide nanostructures [1,3,5,6]. Recently, it was shown that the β phase content of PVDF can be improved introducing CoFe₂O₄ nanoparticles into the polymer and applying a DC magnetic field [25]. This effect has been ascribed to the strong tensile stress at the CoFe₂O₄/PVDF interfaces originating from the interaction between the magnetic field and the CoFe₂O₄ nanoparticles. As a result, a very high β phase content (up to 95%) has been measured in the PVDF nanocomposite with 5 wt % CoFe₂O₄. However, the authors limited the analysis to the β phase content and it was not clear if the β phase increase corresponded to an increase of the piezoelectric coefficient as well. In fact, high values of d_{33} cannot be achieved, in general, with an enhancement of the β phase content only, but they are associated to an alignment of the piezoelectric domains within the material [18].

In this work, we developed and characterized, in terms of piezoelectric coefficient, a novel piezoelectric nanocomposite, based on PVDF-TrFe and CoFe₂O₄ nanoparticles. We adopted PVDF-TrFe instead of PVDF, as in [25], due to its superior β phase content, as discussed above. The PVDF-TrFe/CoFe₂O₄ nanocomposite was poled under different strengths of a DC magnetic field and at different temperatures (room temperature (RT) and 65 °C), in order to enhance the alignment of piezoelectric domains. We demonstrate that this approach is an effective and simple method to improve the piezoelectric response of PVDF-TrFe. The piezoelectric coefficient was evaluated through piezoresponse force microscopy (PFM), which is a very powerful technique to characterize the micro- and nanoscale piezoelectric response of piezoelectric materials [1,2,4,26,27].

Results and Discussion

In order to understand whether the β phase fraction was influenced by magnetic poling, we performed FTIR analyses of six different samples. Figure 1 shows the FTIR spectra of the nanocomposite specimen produced with a CoFe₂O₄ nanoparticle content of 5 wt %, poled for increasing time (from 60 to 120 min) at increasing strengths of the DC magnetic field (50 and 110 mT). As already reported in [1-3,5,6,28], it is possible to determine the relative fraction of the β phase, $F(\beta)$, through the analysis of the peaks at 763 and 840 cm⁻¹, which are char-

acteristic of the α phase and the β phase, respectively. To be more specific, $F(\beta)$ can be estimated by the using following equation [28]:

$$F(\beta) = \frac{A_{\beta}}{(K_{\beta}/K_{\alpha})A_{\alpha} + A_{\beta}}, \quad (1)$$

where A_{α} and A_{β} are the absorbance at 763 and 840 cm^{-1} , respectively, for the α and β phases, and K_{α} and K_{β} are the absorption coefficients at the corresponding wavenumbers (7.7×10^4 and $6.1 \times 10^4 \text{ cm}^2 \cdot \text{mol}^{-1}$, respectively). As it can be seen from Figure 1, the spectra of neat PVDF-TrFE presents two clear features at 763 cm^{-1} and 840 cm^{-1} and, by using Equation 1, we obtained an estimation of $F(\beta) = 81.06\%$. This is higher than the value of $F(\beta)$ of pure PVDF [3] and is in agreement with values reported for PVDF-TrFE in [29]. However, when PVDF-TrFE is filled with CoFe_2O_4 nanoparticles, the measured FTIR spectra show a broadband shoulder close to the α phase peak located at 763 cm^{-1} (probably due to the interaction between polymer and nanoparticles), making the evaluation of the relative fraction of β phase by using Equation 1 difficult. By deconvolving the shoulder from the absorption band related to the α phase centered at 763 cm^{-1} , we estimated for the different samples a value of $F(\beta) = (82 \pm 3)\%$. The relative-

ly large error is due to the uncertainty in the deconvolution procedure. From this estimation, and considering that the intensity of the β phase peaks remains unaffected by the introduction of CoFe_2O_4 nanoparticles as well as by the successive magnetic poling processes, we conclude that the relative fraction of the β phase remains nearly constant upon the introduction of the nanoparticles and it is practically unaffected by the magnetic poling. This is in contrast to what has been reported in [25], where an increase of $F(\beta)$ was observed, with a maximum increase for magnetic fields around 400 Oe.

Furthermore, analyzing the FTIR data in the range of 1600–1900 cm^{-1} , as reported in Figure 1, we observed that a broad peak at 1740 cm^{-1} appears in the spectra of all PVDF-TrFE/ CoFe_2O_4 nanocomposite samples. We attributed this absorption band to carbonyl groups (C=O), in agreement with what has been reported in [30], likely originating from the formation of bonds between O atoms of the CoFe_2O_4 nanoparticles and C atoms of PVDF-TrFE chains.

In order to quantify the piezoelectric response of the PVDF-TrFE/ CoFe_2O_4 nanocomposites we performed PFM. Three different regions of each sample were measured to determine an average piezoelectric coefficient (d_{33}), through a procedure developed to quantitatively evaluate d_{33} [2,3,31]. For neat PVDF-

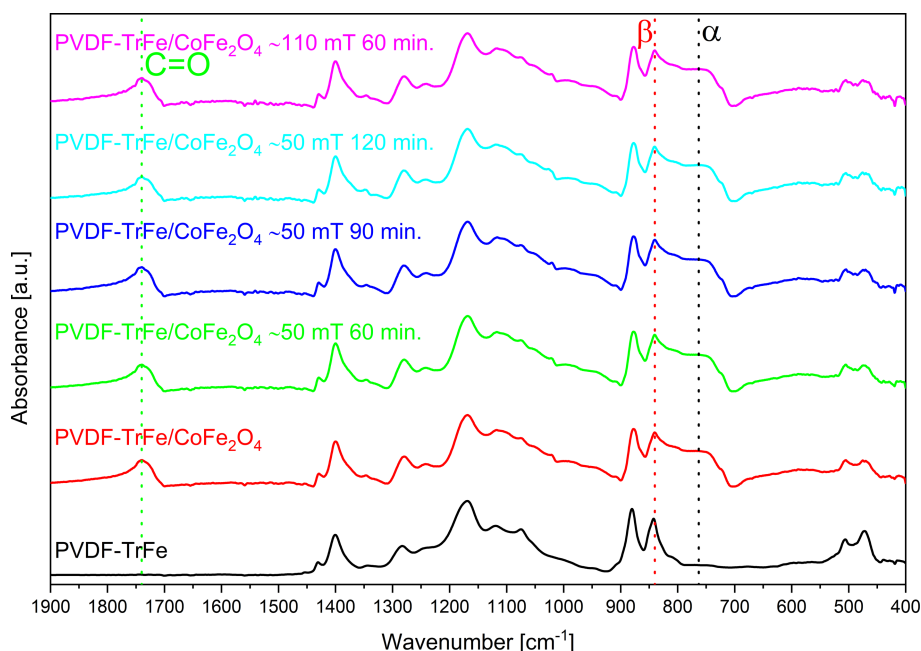
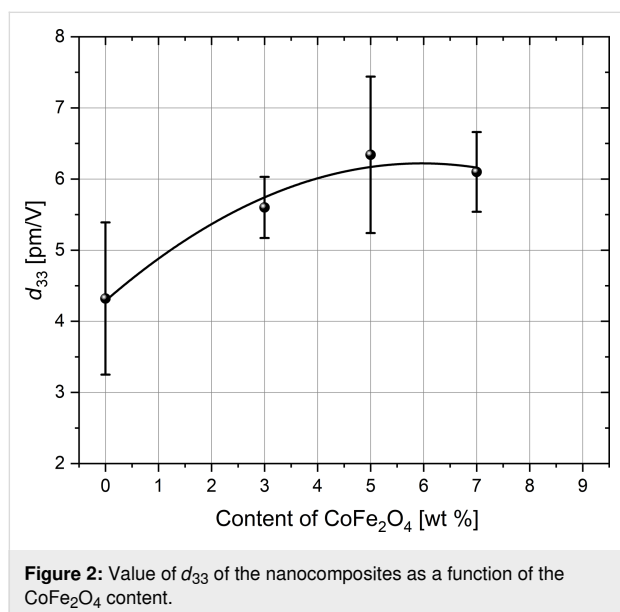


Figure 1: FTIR spectra of the produced samples: i) neat PVDF-TrFE; ii) PVDF-TrFE filled with CoFe_2O_4 nanoparticles at 5 wt %; iii) the PVDF-TrFE filled with CoFe_2O_4 at 5 wt % and poled for 60 min at 65 °C with a magnetic field of 50 mT; iv) the PVDF-TrFE filled with CoFe_2O_4 at 5 wt % and poled for 90 min at 65 °C with a magnetic field of 50 mT; v) the PVDF-TrFE filled with CoFe_2O_4 at 5 wt % and poled for 120 min at 65 °C with a magnetic field of 50 mT; vi) the PVDF-TrFE filled with the CoFe_2O_4 at 5 wt % and poled for 60 min with a magnetic field of 110 mT.

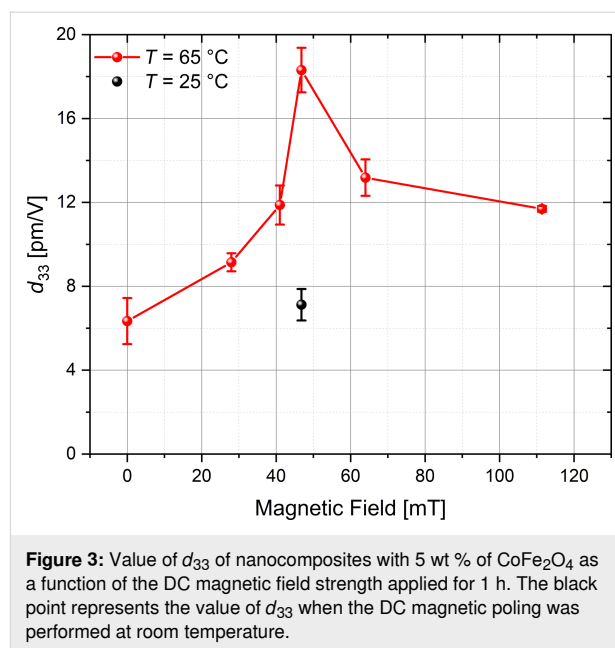
TrFe we obtained $d_{33} = 4.32 \pm 1.07$ pm/V, a much lower value than those obtained after electrical poling ($d_{33} \approx 30$ pm/V) [32,33].

First, we analyzed the piezoelectric response of nanocomposites with different content of CoFe_2O_4 nanoparticles. As shown in Figure 2, d_{33} increases when CoFe_2O_4 nanoparticles are added, showing a maximum of 6.34 ± 1.1 pm/V at 5 wt %, in agreement to what has been reported in [25], where the maximum β phase content was found for a content of nanoparticles of 5 wt %.



After that, we focused our investigation on the effect of DC magnetic poling on nanocomposites with CoFe_2O_4 nanoparticles at 5 wt %. After curing, the spin coated nanocomposite thin films were exposed to a DC magnetic field for 1 h at 65 °C. In Figure 3 the d_{33} values are reported as function of the applied DC magnetic field strength. As can be seen, the piezoelectric coefficient increases when the magnetic field is increased and reaches a maximum value for a magnetic field strength of 50 mT. Also shown in Figure 3 is the d_{33} value of a sample magnetically poled with a field of 50 mT at RT. The value, although higher than that of the un-poled sample, is substantially lower than that of the sample poled with the same magnetic field at 65 °C.

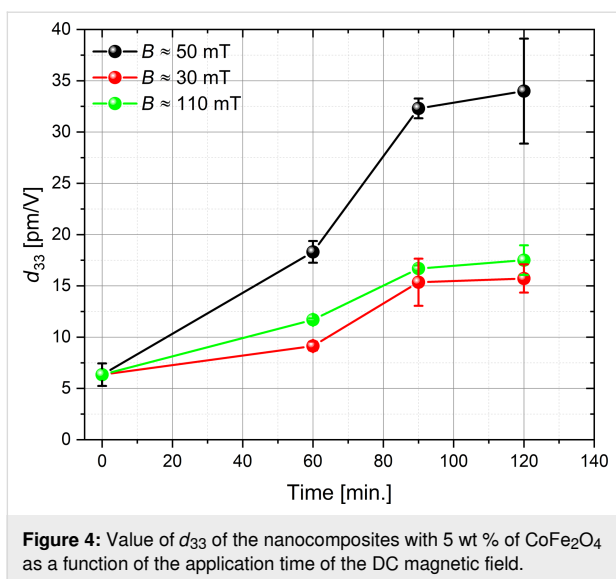
We assume that the d_{33} increase induced by DC magnetic poling was due to the increased alignment of the β phase domains along the magnetic field direction, rather than due to an increase of the β phase content, as proposed in [25]. In particular, we speculate that chemical bonding can take place between PVDF-TrFe and CoFe_2O_4 nanoparticles, with the forma-



tion of a carbonyl group (C=O), as suggested by the FTIR spectra reported in Figure 1. When the DC magnetic field is applied, the ferromagnetic nanoparticles orient themselves along the direction of the applied field and then drag the polymeric chains of PVDF-TrFe to align in the same direction. At relatively high magnetic field strengths ($B > 50$ mT) we found that the d_{33} increase is lower, in agreement with what has been observed in [25]. This behaviour has been attributed to the formation of CoFe_2O_4 nanoparticle aggregates [25]. The presence of these aggregates will be investigated in the following part dealing with the morphological analysis.

Also, temperature plays a relevant role in the orientation of the β phase. As shown in Figure 3, when the DC magnetic poling is performed at RT the value of d_{33} does not increase as much as in the case in which the temperature is kept at 65 °C. Increasing the temperature makes the polymeric nanocomposite softer, thus facilitating the orientation of β phase domains along the magnetic field direction.

We have also investigated the effect of the application time of the DC magnetic field on d_{33} . Figure 4 shows the measured d_{33} values of samples exposed to the magnetic field for increasing periods of time. The d_{33} values tend to saturate after 90 min of magnetic field poling, reaching, in the case of the samples poled with a magnetic field of 50 mT, an average value as high as 34 pm/V. We note that such a value is comparable to or even higher than those reported for electrically poled PVDF-TrFe samples [32,33]. This renders the process of magnetic poling of PVDF-TrFe/ CoFe_2O_4 nanocomposites particularly attractive for applications where electrical poling may have limitations.



In order to verify the presence of the aggregates of the CoFe_2O_4 we investigated the morphology of the CoFe_2O_4 nanoparticles (Figure 5a) and of the PVDF-TrFe/ CoFe_2O_4 nanocomposites (Figure 5b) using field-emission scanning electron microscopy (FESEM). As shown in Figure 5b, the morphology of the produced nanocomposites is homogeneous and it is characterized by spherulitic structures with an average diameter of ca. 1 μm .

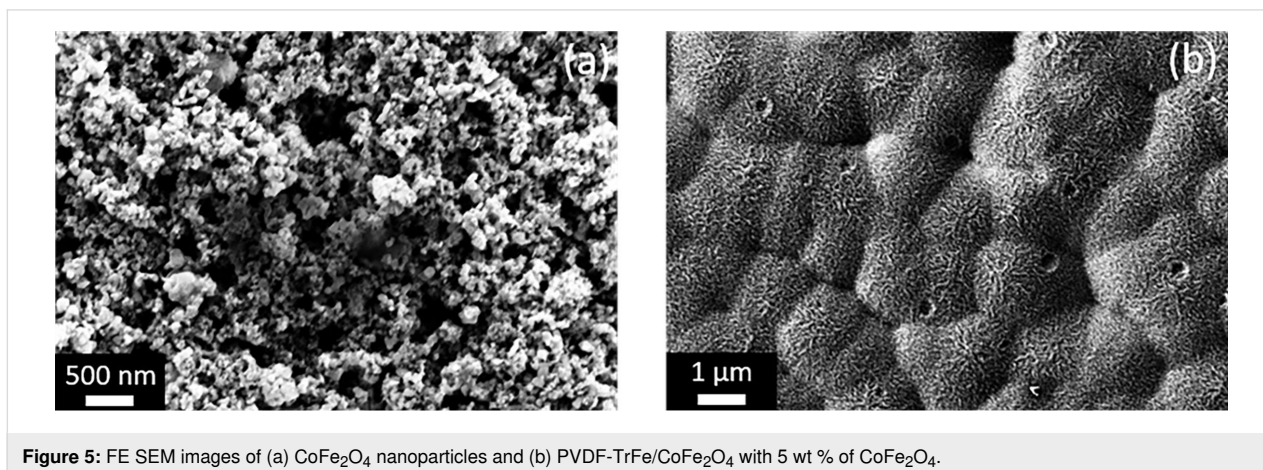
The samples were also measured after magnetic poling under different magnetic field strengths and we did not observe appreciable changes in the spherulitic structure (Figure 6). However, Figure 6b,c shows the aggregation of CoFe_2O_4 nanoparticles in some areas, in analogy with what has been reported in [25]. The formation of aggregates was confirmed by energy-dispersive X-ray spectroscopy (EDX). In correspondence with the agglomeration we observed a higher intensity of the O, Fe, and Co signals, as reported in the chemical maps shown in Figure 7, indicating the presence of clusters of CoFe_2O_4 nanoparticles.

Despite the presence of these agglomerates Fe and Co appear to be uniformly distributed in the nanocomposite film, confirming that the nanoparticles are well dispersed in the polymeric matrix. It should be pointed out that we also observed some smaller aggregates in the un-poled samples, but with a much lower density than in the magnetically poled samples.

Conclusion

In this work we developed a simple and cost-effective method to fabricate a polymeric nanocomposite with high piezoelectric coefficient by adding ferromagnetic CoFe_2O_4 nanoparticles to PVDF-TrFe and performing magnetic poling. The highest d_{33} value, up to 39 pm/V, was obtained after adding 5 wt % of CoFe_2O_4 nanoparticles and applying a DC magnetic field of 50 mT. Application of the magnetic field produced an alignment of the β phase along the direction of the applied magnetic field rather than an increase of the β phase content itself.

We believe that the increase of the d_{33} is due to the strong interaction between the molecular chains of the polymer nanocomposite and the magnetic field, thanks to the drag effect produced by the CoFe_2O_4 nanoparticles, which are strongly anchored to PVDF-TrFe. In fact, based on the FTIR analysis of the produced samples, showing the appearance of an absorption band attributed to carbonyl groups (C=O) when the CoFe_2O_4 nanoparticles are introduced, we propose that chemical bonds are formed between O atoms of the CoFe_2O_4 nanoparticles and C atoms of PVDF-TrFe chains. When the DC magnetic field is applied, the orientation of the CoFe_2O_4 nanoparticles drags the polymeric chains along the direction of the applied field. We observed that the maximum value of d_{33} was reached when a DC magnetic field of 50 mT was applied, while for higher values of magnetic fields the d_{33} value tends to decrease. This could be due to the aggregation of the CoFe_2O_4 nanoparticles forced by intense magnetic fields, resulting in a reduced alignment efficiency of the polymeric chains, as suggested in [25].



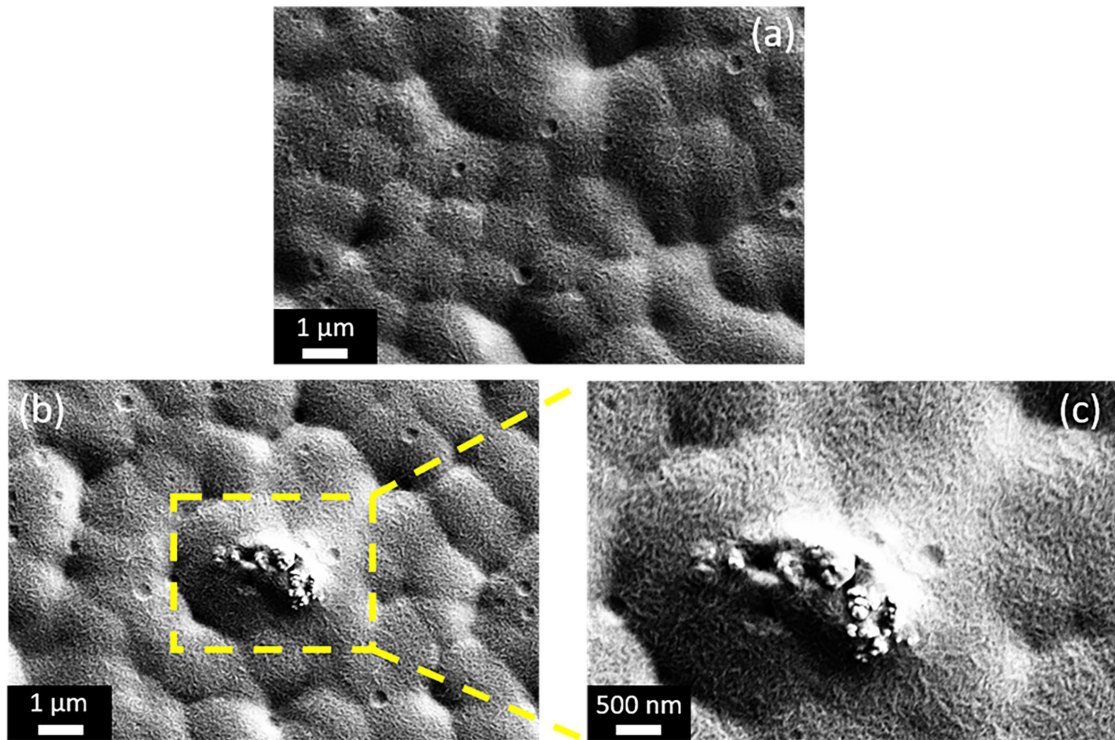


Figure 6: FESEM images of PVDF-TrFe/CoFe₂O₄ nanocomposites with 5 wt % of CoFe₂O₄ magnetically poled at 111 mT for 1 h at 65 °C.

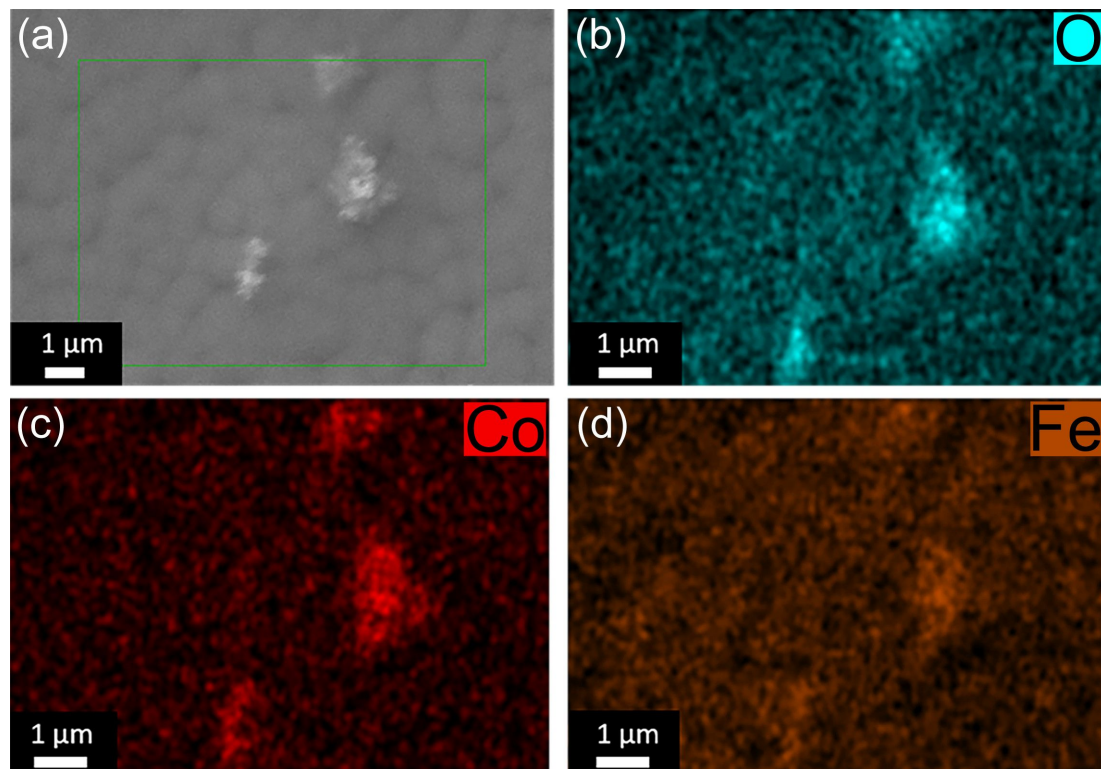


Figure 7: (a) SEM image and (b–d) EDX maps of (b) oxygen, (c) cobalt, and (d) iron of the PVDF-TrFe/CoFe₂O₄ nanocomposite with 5 wt % of CoFe₂O₄ magnetically poled at 111 mT for 1 h at 65 °C.

The FTIR measurements of PVDF-TrFe/CoFe₂O₄ nanocomposites showed a broadband shoulder close to the α phase peak located at 763 cm⁻¹, making the evaluation of the β phase difficult. Nevertheless, deconvolving the shoulder from the absorption band related to the α phase we estimated for the different samples a relative fraction of the β phase of $F(\beta) = (82 \pm 3)\%$. From this estimation, and considering that the intensity of the β phase peaks remains nearly unaffected by the introduction of CoFe₂O₄ nanoparticles as well as by the successive magnetic poling processes, we conclude that the relative fraction of the β phase remains nearly constant. This implies that the primary effect of the DC magnetic poling is to increase the orientation of the β phase domains along the magnetic field direction, rather than to increase the β phase content, as proposed in [25].

The developed combination of polymeric nanocomposite, including ferromagnetic CoFe₂O₄ nanoparticles, and the application of a DC magnetic poling provides an alternative route to obtain highly efficient piezoelectric materials with excellent d_{33} values, avoiding electrical poling or mechanical stretching. This process may be particularly attractive in the fabrication of energy harvesting devices or wearable sensors for flexible electronics applications.

Experimental

The PVDF-TrFe/CoFe₂O₄ nanocomposite thin films were produced through spin coating. The CoFe₂O₄ nanoparticles (Sigma-Aldrich, 99%) were dispersed in *N,N*-dimethylformamide (DMF, Sigma-Aldrich, $\geq 99\%$) with a concentration of 1 wt % and tip-sonicated using an ultrasonic processor in pulsed mode for 20 min at 70% of the power amplitude. Subsequently, the CoFe₂O₄ suspension was added to a PVDF-TrFE solution (Piezotech FC Ink L, 7 wt %) at the desired ratio. The mixture

was bath-sonicated for 30 min and then spin coated (30 s with a spin speed of 2000 rpm) onto polyethylene terephthalate/indium tin oxide (PET/ITO, Sigma-Aldrich, $R_s = 60 \Omega/\text{sq}$).

The obtained melt was cured in the oven at 120 °C for 2 h. After curing, the nanostructured thin film was placed over a heated mat reaching 65 °C and a DC magnetic field was applied through a ferromagnetic core (Figure 8).

The morphology of the PVDF-TrFe/CoFe₂O₄ nanocomposite thin films was investigated using a field-emission scanning electron microscope (FESEM, Auriga, Carl Zeiss) operated with an accelerating voltage of 5 kV. Chemical composition analysis was performed through EDX using the FESEM, equipped with a Bruker Quantax EDX setup capable of an energy resolution of 123 eV at Mn K α . In order to prevent charging the samples were metalized with 20 nm of Cr using a Quorum Technologies Q150T ES sputter coater.

All FTIR absorption spectra were recorded at RT using a FTIR spectrometer (Vertex 70 by Bruker Optics GmbH) equipped with a single reflection diamond ATR cell. The analyses were performed in the typical mid-IR spectral range (4000–400 cm⁻¹) at a resolution of 2 cm⁻¹ and with 256 scans.

The piezoelectric coefficients were measured through PFM [1,5,27] using a commercial Bruker-Veeco Dimension Icon AFM with a Co/Cr-coated-tip silicon cantilever (MESP-RC-V2, Bruker). Following the procedure described in [2,3], we scanned three different areas, $5 \times 5 \mu\text{m}^2$ in size, of each sample, with 256×256 acquisition points per scanning area using a scan rate of 0.5 Hz. An alternating voltage with a frequency of 15 kHz was applied to the tip.

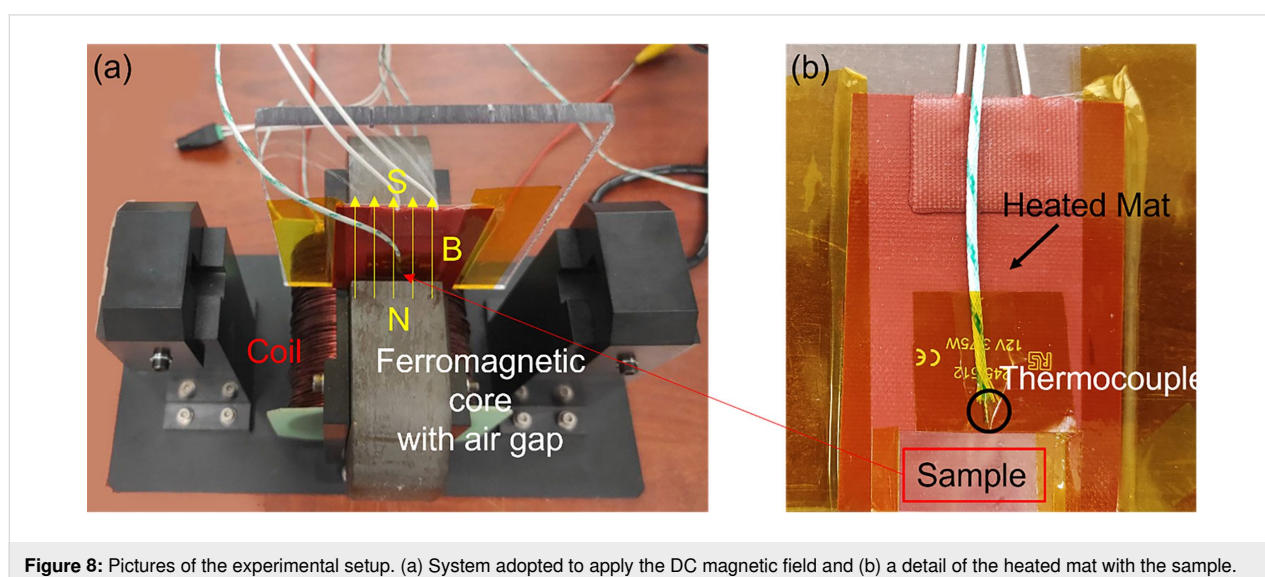


Figure 8: Pictures of the experimental setup. (a) System adopted to apply the DC magnetic field and (b) a detail of the heated mat with the sample.

In order to obtain a quantitative evaluation of d_{33} , the amplitude of the PFM signal is measured as function of the applied voltage V_{ac} in the selected range of 1–5 V. First, a calibration sample of periodically poled lithium niobate (PPLN), with a known value of the piezoelectric coefficient ($d_{33PPLN} = 7.5$ pm/V), is measured. Then, the sample under investigation is tested and the PPLN is measured again. The two piezoelectric calibration signals of PPLN are compared for each value of the applied voltage V_{ac} . If the difference between them is less than 20%, the measurement of the sample under test is considered reliable [2,3].

The calibration factor $\xi = m_{PPLN}/d_{33PPLN}$ (in which m_{PPLN} is the slope of the straight line of the amplitude of the PFM signal vs V_{ac} , and d_{33PPLN} is the known piezoelectric coefficient of PPLN) is evaluated, averaging over the two calibration measurements. The d_{33} value of the sample under test is finally calculated using the following expression:

$$d_{33} = m = \frac{V_{\text{sample}}}{\xi V_{ac}}, \quad (2)$$

in which V_{sample} is the PFM signal of the sample under test.

PFM measurements were performed on three different areas for each sample and two samples for each condition were tested. We determined the average PFM response and the corresponding standard deviations, which are reported as error bars in Figures 2–4.

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