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Enhancement of Piezoelectric Coefficient (d_{33}) 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 a considerable interest to develop energy harvesters and sensors. Among the piezoelectric materials, a special focus was paid on electroactive polymers such as Poly(vinylidene fluoride) [PVDF] and on its copolymer Poly(vinylidene fluoride-co-trifluoroethylene) [PVDF-TrFe], which is one of the most investigated piezoelectric polymers, due to the high β -phase content resulting under specific curing or processing conditions. However, to get high piezoelectric coefficient (d_{33}), alignment of the β -phase domains is needed, which is usually obtained by applying a high electric field at moderate temperatures. This process, usually referred as electrical poling, requires the deposition of contact electrodes over 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 a top electrode and 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.

Keywords

PVDF-TrFe; CoFe₂O₄; PVDF-TrFe nanocomposites; Magnetic Poling; Piezoelectric Effect; Piezoresponse Force Microscopy (PFM)

Introduction

In the last years, innovative energy harvesting systems based on the piezoelectric effect, able to convert the 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, lithium niobate, which have a high piezoelectric constant and therefore a high conversion efficiency. However, these materials are toxic, brittle and they are not environmental 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 fabrication of flexible piezoelectric nanogenerator [1–7].

One of the most investigated piezoelectric polymers is the 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 polymorphs phases: 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 an electric

poling. The β phase, the so called TTT (all trans) planar zigzag chain conformation, is the one originating the electroactive response of the polymer, being the polar phase that shows the strongest ferro-, piezo-, pyroelectric behavior [13], due to its largest spontaneous polarization (7×10^{-30} C·m) [14]. In order to obtain a high content of β phase, PVDF is generally polymerized with trifluoroethylene (TrFe), producing the so called copolymer of PVDF, i.e. the so called Poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) [15–17]. This copolymer shows a higher piezoelectric coefficient compared with PVDF, still maintaining a high flexibility, sensitivity and mechanical durability and even resulting, like the PVDF, a bio-compatible polymer. In order to obtain the best piezoelectric response, dipoles in PVDF/PVDF-TrFe must be oriented along a preferential direction. The dipoles orientation is generally obtained by electrical poling. This process consists in the application of a strong DC electric field ($\sim 10^6$ V/m) at elevated temperature (~ 120 °C) through a top and bottom electrode [18]. However, this technique is not cost effective and it 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 in PVDF, such as mechanical stretching [19,20], spin-coating [17], quenching [18], combination of these latter two techniques [2], addition to the PVDF matrix external additives such as metal nanocomposites [14,23], ceramic filler [24], graphene nanoplatelets (GNPs) and their combination with zinc oxide nanostructure [1,3,5,6]. Recently, it was shown that the β -phase content of PVDF can be improved introducing CoFe_2O_4 nanoparticles into the polymer and applying a DC magnetic field [25]. This effect has been ascribed to the strong tensile stresses at the CoFe_2O_4 /PVDF interfaces originated by the interaction between the magnetic fields and the CoFe_2O_4 nanoparticles. As a result, a very high β -phase content (up to 95%) has been estimated in the PVDF nanocomposite with 5 wt.% CoFe_2O_4 . 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 CoFe_2O_4 nanoparticles. We adopted PVDF-TrFe instead of PVDF, as in Ref. [25], due to its superior β -phase

content, as discussed above. The PVDF-TrFe/CoFe₂O₄ nanocomposite was poled under different levels of DC magnetic field and at different temperatures (room temperature (RT) and 65°C), in order to enhance alignment of piezoelectric domains. We demonstrated that this approach resulted as an effective and simple method to improve the piezoelectric response of PVDF-TrFe. The piezoelectric coefficient was evaluated through the Piezoresponse Force Microscopy (PFM), which is a very powerful technique to characterize the micro- and nano-scale piezoelectric response of piezoelectric material samples [1,2,4,26,27].

Results and Discussion

In order to understand whether the β -phase fraction was influenced by magnetic poling, we performed the FT-IR analysis of six different samples. Figure 1 shows the FT-IR spectra of the nanocomposite specimen produced with a CoFe₂O₄ nanoparticles content of 5 wt.%, and poled for increasing time (from 60 min to 120 min) at increasing intensities of DC magnetic field (i.e 50 mT and 110 mT).

As already reported in [1–3,5,6,28,29], it is possible to determine the relative fraction of the β phase, $F(\beta)$, through the analysis of the peaks at 763 cm⁻¹ and 840 cm⁻¹, which are characteristic of the α - and β -phases respectively. In particular, $F(\beta)$ 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 cm⁻¹ and 840 cm⁻¹, for the α - and β -phases, and K_{α} and K_{β} are the absorption coefficients at their corresponding wavenumbers (7.7*10⁴ cm²/mol and 6.1*10⁴ cm²/mol, respectively). As it can be seen from the data reported in Figure 1, the spectra of neat PVDF-TrFE presented two clear features at 763 cm⁻¹ and 840 cm⁻¹ and, by using eq. 1, we obtained an estimation of $F(\beta) = 81.06\%$ which is higher than the value of $F(\beta)$ of pure PVDF [3] and is in agreement with values reported for PVDF-TrFe in [30]. However, when the PVDF-TrFe is filled with CoFe₂O₄ nanoparticles, the measured FT-IR 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 difficult the evaluation of the relative fraction of β -

phase by using eq. 1. By deconvolving the shoulder from the absorption band related to the α -phase centered at 763 cm^{-1} , we estimated for the different samples an $F(\beta) = (82 \pm 3)\%$. The relatively large error is due to the uncertainty in the deconvolution procedure. From this estimation and considering that the intensity of the β -peaks remain 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 reported in ref. [25], where an increase of the $F(\beta)$ was observed, with a maximum increase for magnetic fields around 400 Oe .

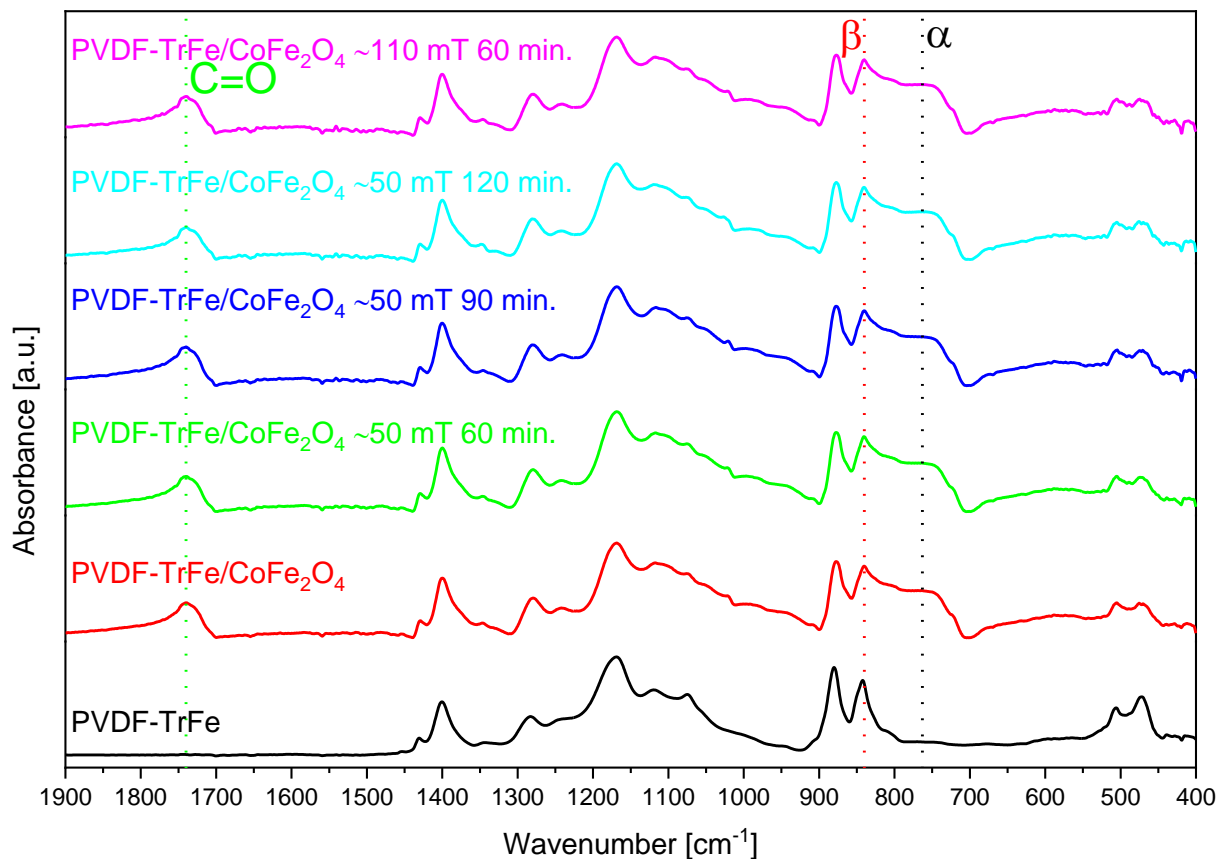


Figure 1: FT-IR spectra of the produced samples: i) neat PVDF-TrFE; ii) PVDF-TrFe filled with CoFe_2O_4 nanoparticles at 5 wt.%; iii) the PVDF-TrFe filled with CoFe_2O_4 at 5 wt.% and poled for 60 min with a magnetic field of 50 mT; iv) the PVDF-TrFe filled with CoFe_2O_4 at 5 wt.% and poled for 90 min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

Furthermore analyzing the FT-IR measured data in the range of $(1600-1900) \text{ cm}^{-1}$, 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 ($\text{C}=\text{O}$), in agreement with what reported in [31], and likely due to the formation of bonds between the O atoms of the CoFe_2O_4 nanoparticles and the C atoms of PVDF-TrFe chains.

In order to quantify the piezoelectric response of the PVDF-TrFe/ CoFe_2O_4 nanocomposites, we performed the piezoresponse force microscopy (PFM). Three different regions of each sample were measured to determine an average piezoelectric coefficient (d_{33}), through a procedure developed to quantitatively evaluate the d_{33} [2,3,32]. For the neat PVDF-TrFe we obtain a $d_{33} = (4.32 \pm 1.07) \text{ pm/V}$, a much lower value if compared to those that can be obtained after electrical poling ($d_{33} \sim 30 \text{ pm/V}$), [33,34].

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

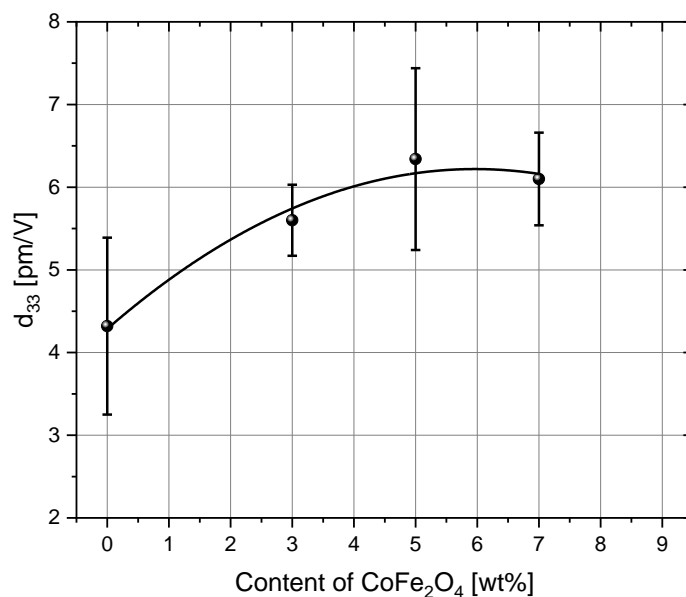


Figure 2: d_{33} value of the nanocomposites as a function of CoFe_2O_4 content.

Then we have 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 subjected to DC magnetic field for 1 h at 65 °C. In Figure 3 the d_{33} values are reported for different applied DC magnetic field intensities. As can be seen, the piezoelectric coefficient increases when the magnetic field is increased and reaches a maximum value for a magnetic field 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 but at 65°C.

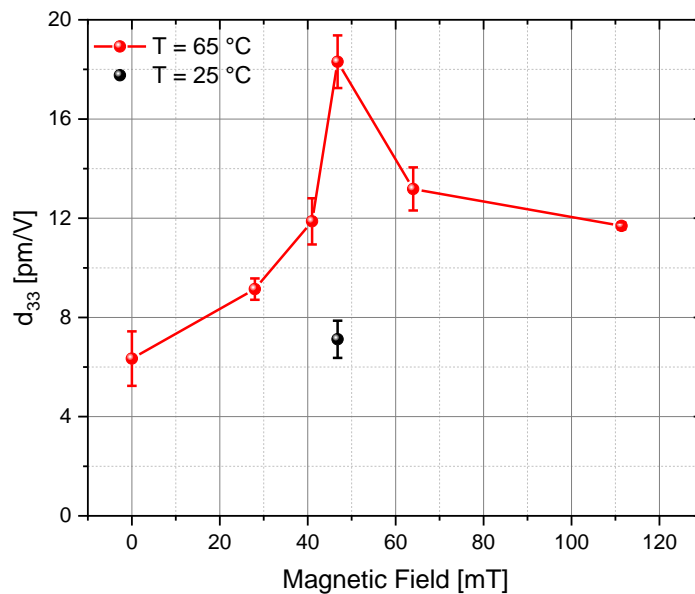


Figure 3: d_{33} value of the nanocomposites with 5 wt.% of CoFe_2O_4 as a function of the DC magnetic field applied for 1h. The black point represents the value of the d_{33} when the DC magnetic poling was performed at room temperature.

We interpret that the d_{33} increase induced by the DC magnetic poling was due to the increased alignment of the β -phase domains along the magnetic field direction, rather than to an increase of the β -phase content, as proposed in Ref. [25]. In particular, we

speculate that chemical bonding can take place between the PVDF-TrFe and CoFe_2O_4 nanoparticles, with the formation of a carbonyl group ($\text{C}=\text{O}$), as suggested by FT-IR spectra reported in Figure 1b. . 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 the PVDF-TrFe to align in the same direction. At relatively high magnetic field ($B > 50$ mT) we found that the d_{33} increase is lower, in agreement with what observed in [25]. This behaviour has been attributed to the formation of CoFe_2O_4 nanoparticles aggregates [25]. The presence of these aggregates was confirmed in the following part dealing with the morphological analysis. It should be also noticed the relevant role that the temperature plays in the orientation of the β phase: as shown in Figure3, when the DC magnetic poling is performed at RT the d_{33} does not increase as much as in the case in which the temperature is kept at 65°C . Indeed, increasing temperature makes the polymeric nanocomposite softer, thus facilitating the β -phase domain orientation along the magnetic field direction.

We have also investigated the effect of the application time of the DC magnetic field on the d_{33} . Figure 4 shows the measured d_{33} on samples exposed to magnetic field for increasing time durations. As it can be observed, 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 or even higher than those reported for PVDF-TrFe samples electrically poled [33,34], making the process of magnetic poling of PVDF-TrFe/ CoFe_2O_4 nanocomposite particularly attractive for those applications where electrical poling may have limitations.

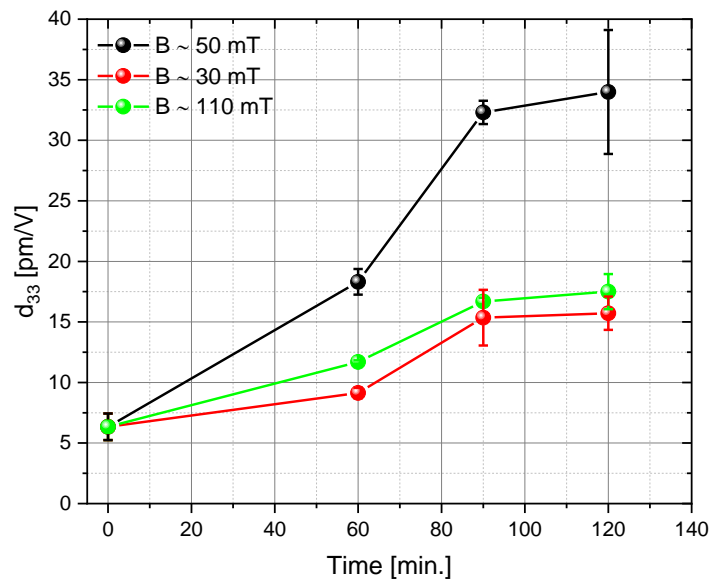


Figure 4: d_{33} value of the nanocomposites with 5 wt.% of CoFe_2O_4 as a function of the application time of the DC magnetic field.

In order to verify the presence of the aggregates of the CoFe_2O_4 we investigated the morphology of the CoFe_2O_4 nanoparticles and of the PVDF-TrFe/ CoFe_2O_4 nanocomposites through a Field Emission Scanning Electron Microscope (FE-SEM). As showed in Figure 5 (b) the morphology of the produced nanocomposites is homogeneous and it is characterized by spherulitic structures with an average diameter of $\sim 1 \mu\text{m}$.

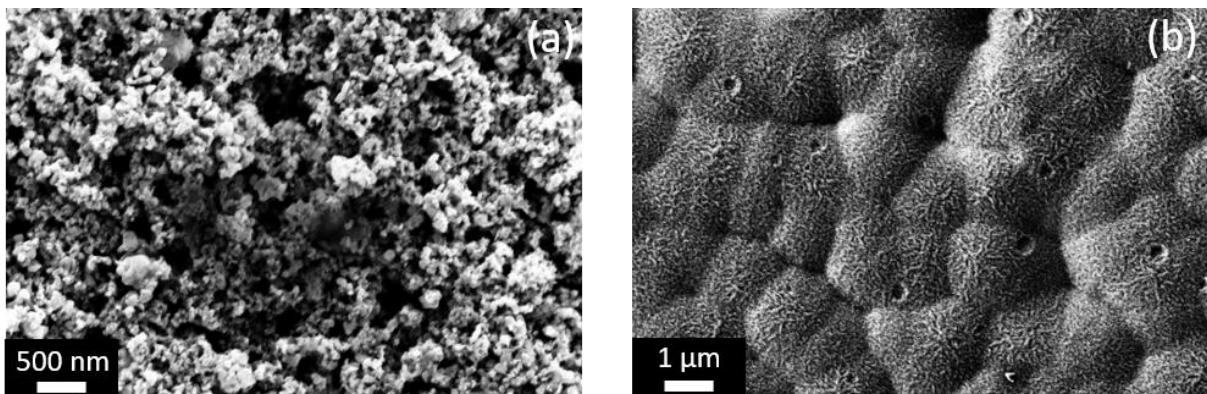


Figure 5: FE-SEM images of the (a) CoFe_2O_4 nanoparticles; (b) and PVDF-TrFe/ with 5 wt.% of CoFe_2O_4 .

The samples were also measured after magnetic poling under different magnetic field intensity and we did not observe appreciable changes in the spherulitic structure (see Fig 6).

However, as showed in Figure 6 (b) and (c), we observed the aggregation of CoFe_2O_4 nanoparticles in some areas, in analogy with what reported in [25]. The formation of aggregates was confirmed by Energy Dispersive X-ray analysis (EDX): indeed, 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, as can be seen from Figure 7, Fe and Co appear to be uniformly distributed in the nanocomposite film, confirming that the nanoparticles are well dispersed in the polymeric matrix.

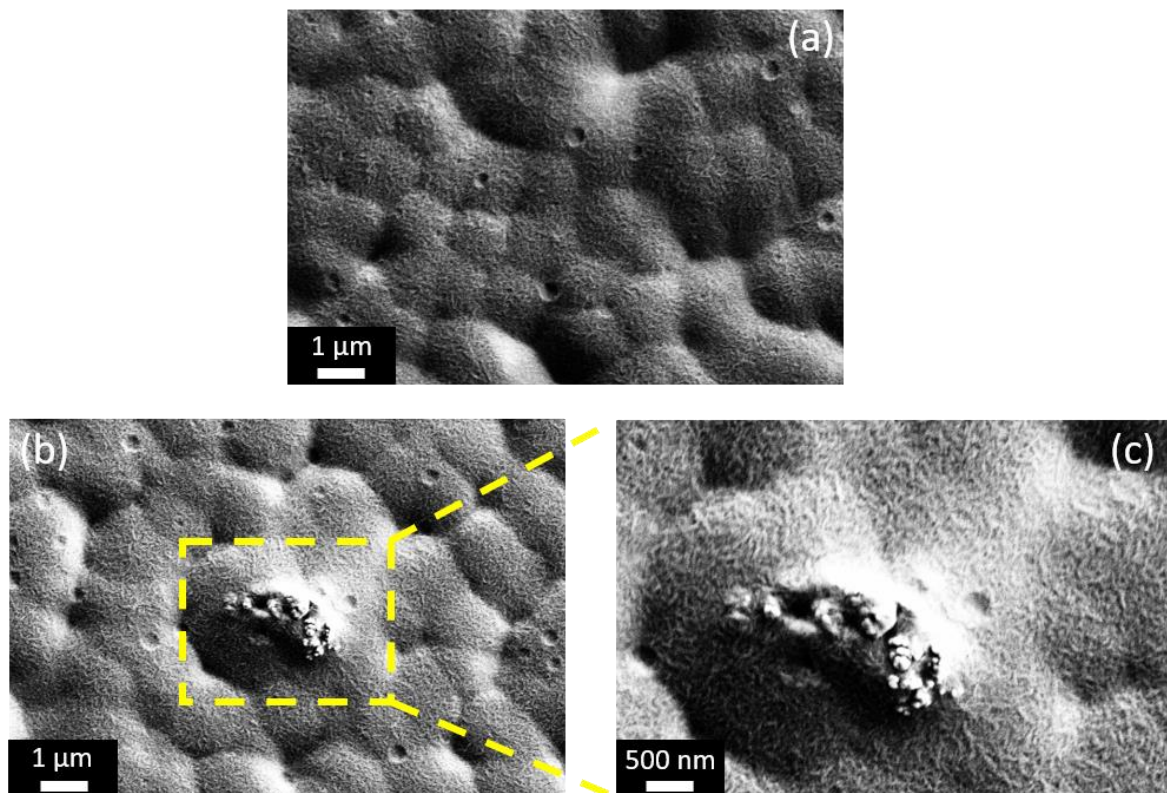


Figure 6: FE-SEM images of the PVDF-TrFe/ CoFe_2O_4 nanocomposites with 5 wt.% of CoFe_2O_4 magnetically poled at 111 mT for 1 h at 65 °C.

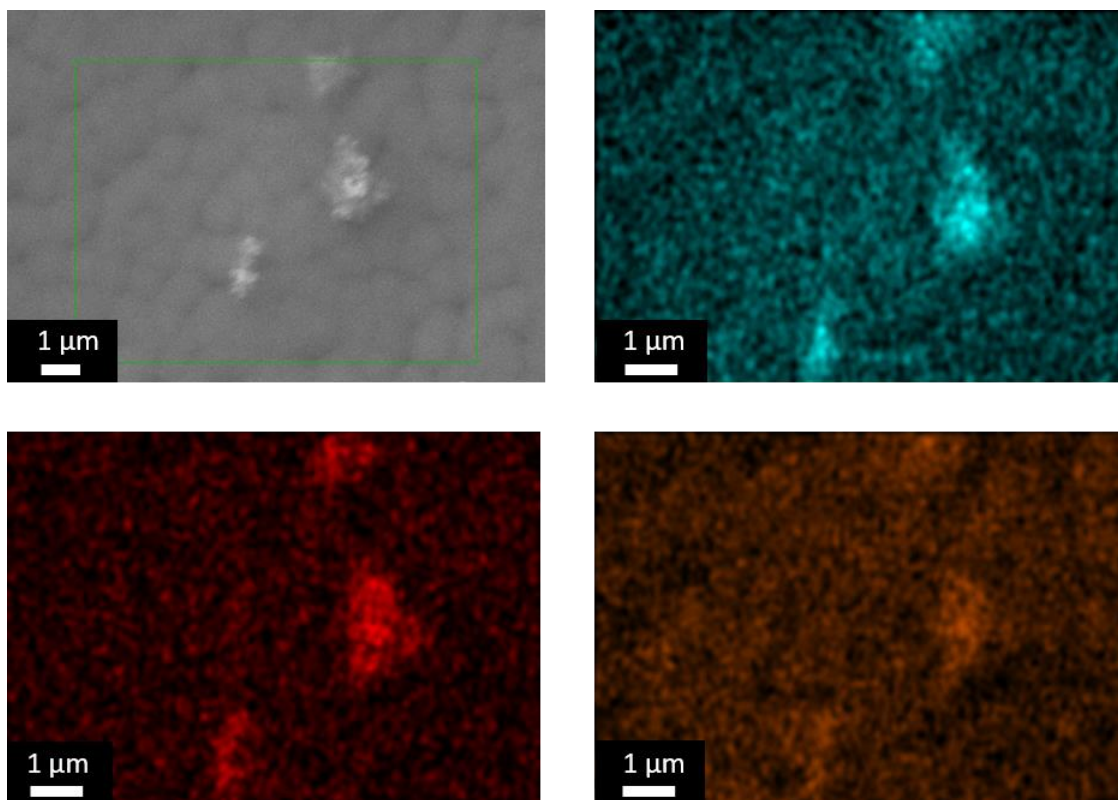


Figure 7: EDX images of the PVDF-TrFe/CoFe₂O₄ nanocomposites with 5 wt.% of CoFe₂O₄ magnetically poled at 111 mT for 1 h at 65 °C.

Conclusion

In this work we developed a simple and cost effective method to fabricate a polymeric nanocomposite with high piezoelectric coefficient by adding ferromagnetic CoFe₂O₄ nanoparticles to PVDF-TrFe and performing magnetic poling. The highest d_{33} value, up to 39 pm/V, was obtained introducing 5 wt% of CoFe₂O₄ 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 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 CoFe₂O₄ nanoparticles, which are strongly anchored to PVDF-TrFe. In fact, based on the FT-IR analysis of the produced samples, showing the appearance of an absorption band due to the carbonyl groups (C=O) when the CoFe₂O₄ nanoparticles are introduced, we propose that chemical bonds are formed between the O atoms of the CoFe₂O₄ nanoparticles and the C atoms of PVDF-TrFe

chains. When the DC magnetic field is applied, orientation of the CoFe₂O₄ 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} tends to decrease. This could be due to the aggregation of the CoFe₂O₄ nanoparticles forced by intense magnetic fields, resulting in a reduced alignment efficiency of the polymeric chains, as suggested in [25].

The FT-IR measurements of PVDF-TrFe/CoFe₂O₄ nanocomposites showed a broadband shoulder close to the α -phase peak located at 763 cm⁻¹, making difficult the evaluation of the β -phase. Nevertheless, deconvolving the shoulder from the absorption band related to the α -phase we estimated for the different samples an $F(\beta) = (82 \pm 3) \%$. From this estimation and considering that the intensity of the β -peaks remain 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 Ref. [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 by spin coating process. 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 minutes at 70% of power amplitude. Subsequently the CoFe₂O₄ suspension was added into PVDF-TrFE solution (Piezotech FC Ink L, 7 wt%) at the desired ratio. The mixture was bath

sonicated for 30 minutes 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 so obtained melt was cured in the oven at 120 °C for 2h. After the curing the nanostructured thin film was placed over an heated mat, reaching 65°C and a DC magnetic field was applied through a ferromagnetic core (see Figure 8).

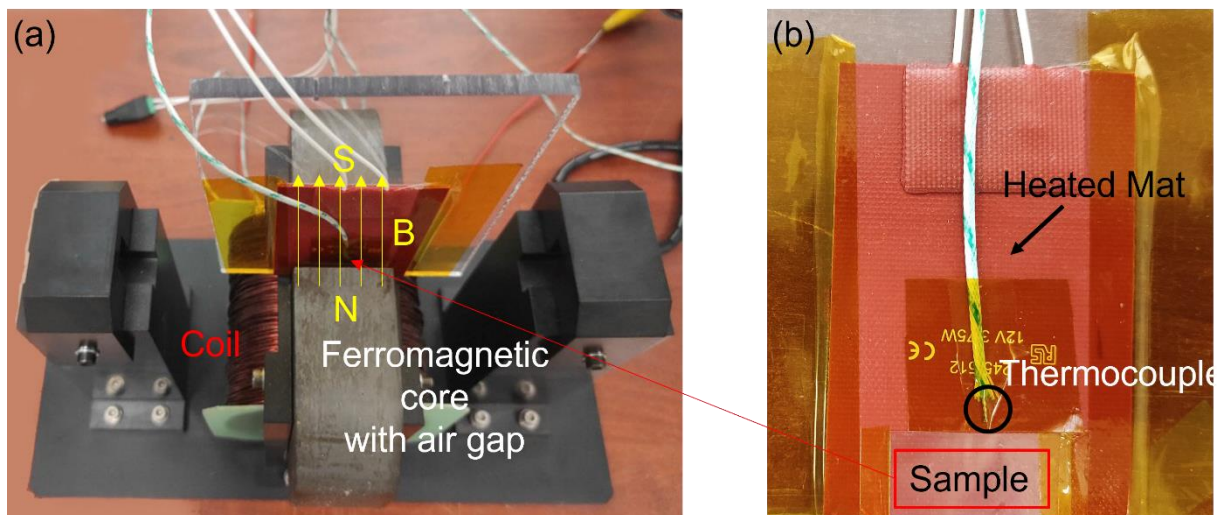


Figure 8: Pictures of the experimental setup. (a) System adopted to apply the DC magnetic field and (b) a detail of the heated mat with the sample.

The morphology of the PVDF-TrFe/CoFe₂O₄ nanocomposite thin films was investigated through a Field Emission Scanning Electron Microscope (FE-SEM, Auriga, Carl Zeiss) operating with an accelerating voltage of 5 kV. Chemical composition analysis was performed through EDX using the FE-SEM, equipped with a Bruker Quantax EDX 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, through a Quorum Technologies Q150T ES sputter coater.

All the FTIR absorption spectra were recorded using a FT-IR spectrometer (Vertex 70 by Bruker Optics GmbH) equipped with a single reflection diamond ATR cell. The analyses were performed into 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 3 different areas (5 x 5) μm^2 in size of each sample, with 256 x 256 acquisition

points per scanning area, and applying an alternating voltage applied to the tip with a frequency of 15 kHz and using a scan rate of 0.5 Hz.

In order to obtain a quantitative evaluation of the d_{33} the amplitude of the PFM signal is measured as function of the applied voltage V_{ac} in the selected range: (1-5) V. At first a calibration sample of a 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. Therefore, the two piezoelectric calibration signals of the PPLN are compared each other, for each value of the applied voltage V_{ac} , and 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 the 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:

$$d_{33} = m = \frac{V_{sample}}{\xi V_{ac}} \quad (1)$$

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

Once the PFM measurements were performed in each selected areas of the sample, we estimated the average PFM response.

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