

Flexible Nanogenerators based on Piezoelectric PVDF-TrFE Nanocomposites Poled by DC Magnetic Field

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Abstract - In the present work we developed a flexible nanogenerator based on PVDF-TrFE/CoFe₂O₄ nanocomposite. In particular, a DC magnetic poling was applied in order to align the β phase. We observed that it is possible to increase the piezoelectric coefficient through magnetic poling. The great advantage of the magnetic poling, with respect to the more conventional electric poling, is that it does not require the use of electrodes, making it a process easier to be industrialized. In this work we obtained a d_{33} value up to 34 pm/V by applying a magnetic field of 50 mT. Magnetically poled PVDF-TrFE/CoFe₂O₄ nanocomposite is then suitable to fabricate highly efficient devices for energy harvesting and wearable sensors. We demonstrated that a flexible nanogenerator can be realized using the magnetically poled nanocomposite and a multilayer-graphene/gold as top electrode. The produced nanogenerators, tested through a commercial mini-shaker, showed a $d_{33} = 34$ pm/V, in good agreement with the average value ($d_{33} = (33.99 \pm 5.12)$ pm/V) measured by PFM directly on the nanocomposite.

Keywords: Nanogenerators; PVDF-TrFE nanocomposites; CoFe₂O₄; magnetic poling; piezoelectric effect; piezoresponse force microscopy (PFM).

1. Introduction

The possibility to convert the vibrational mechanical energy into electric energy, thanks to the development of innovative energy harvesting devices based on the piezoelectric effect, has recently attracted the interest of the scientific community. The higher the piezoelectric coefficients (d_{33}) is, the higher is the conversion efficiency, thus justifying the use of piezoceramics with high d_{33} in piezoelectric devices. However, these materials are toxic, brittle and they are not environmental friendly. In order to overcome these disadvantages, several research group have started to investigate piezoelectric polymers, piezoelectric nanostructures and piezoelectric nanocomposites, showing interesting piezoelectric properties, suitable for fabrication of flexible nanogenerator [1]–[7].

Poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) is one of the most investigated piezoelectric polymers, due to its excellent piezoelectric and ferroelectric properties, high chemical resistance, high thermal stability, large polarization, short switching time and mechanical flexibility. Such properties make it suitable for a wide range of advanced applications, from sensing to energy harvesting [8], [9]. One of the crucial aspects, to obtain high piezoelectric coefficient (d_{33}), is the orientation, along a preferential direction, of the PVDF-TrFE dipoles. Usually, in order to align the electroactive phase, an electrical poling is applied. This process consists in the application of a strong DC electric field ($\sim 10^6$ V/m) at elevated temperature (~ 100 °C) through top and bottom electrodes [10]. However, this technique is not cost effective and it is not easy to be implemented industrially, since it requires the application of a high voltage on each individual device. Recently, alternative techniques such as mechanical stretching [11], spin-coating [12], quenching [13], a combination of the latter two techniques [2] and the addition of external additives such as metal nanocomposites [14], [15], ceramic filler [16], graphene nanoplatelets (GNPs) and their combination with zinc oxide nanostructure [1], [3], [5], [6] have been investigated to enhance the piezoelectric response of the polymer. Furthermore, we have recently reported [17] that by introducing ferromagnetic nanoparticles in PVDF-TrFE/CoFe₂O₄ nanocomposites the d_{33} can be substantially enhanced by applying a DC magnetic poling.

In this work we demonstrate flexible nanogenerators based on PVDF-TrFE/CoFe₂O₄ nanocomposites with a multilayer-graphene/gold top electrode (MGGE). The device has been electromechanically tested by applying perpendicular force with

a commercial mini-shaker and the voltage produced by the piezoelectric effect was monitored by a digital oscilloscope. The nanogenerator exhibits enhanced piezoelectric properties, reaching a final piezoelectric coefficient d_{33} of 34 pm/V, in good agreement with the average value obtained by Piezoresponse Force Microscopy (PFM) $d_{33} = (33.99 \pm 5.12)$ pm/V.

2. Results and discussions

2.1. Fabrication of PVDF/CoFe₂O₄ Nanogenerator

Spin coating process was used to fabricate the PVDF-TrFE/CoFe₂O₄ nanocomposite thin films [17]. A suspension of 1 wt% of CoFe₂O₄ nanoparticles and DMF was tip sonicated. The DMF/CoFe₂O₄ solution was added into PVDF-TrFE ink (Piezotech FC Ink L) at the desired ratio. The mixture was bath sonicated for 30 minutes and then spin coated onto PET/ITO. The obtained film was cured at 120 °C for 2h in an oven. After curing, magnetic poling of the nanostructured thin film was performed by applying a DC magnetic field, generated by a ferromagnetic core, while keeping the film temperature at 65 °C, through a heating mat. Once that the active layer of PVDF-TrFE/CoFe₂O₄ was produced, a multilayer-graphene paper, developed using the procedure described in [18], was sputter coated with 20 nm of Cr and 60 nm of Au and used as top electrode of the device. The multilayer-graphene paper was coated with a Cr/Au layer to increase the conductivity of the electrode, as reported in [4]. In Figure 1 schematic representation (a) and picture (b) of the NG are reported.

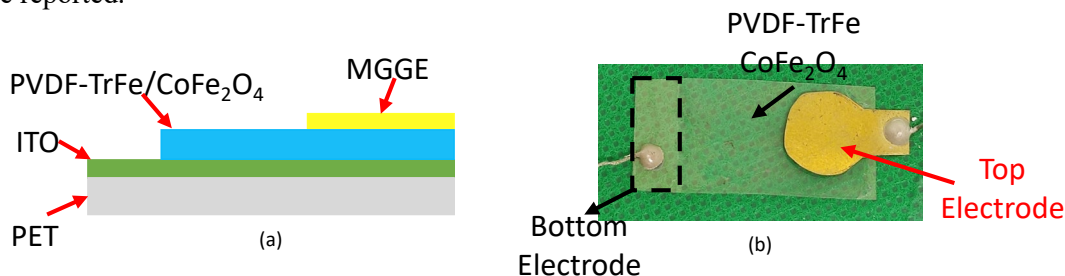


Figure 1 Schematic representation (a) and a picture (b) of PVDF-TrFE/CoFe₂O₄ nanogenerator.

2.2. Morphological Characterization

Field Emission Scanning Electron Microscope (FE-SEM) was used to investigate the morphology of the produced PVDF-TrFE/CoFe₂O₄ nanocomposite. A homogenous Cr layer of 20 nm thickness was sputter coated on the samples in order to prevent charging during the SEM imaging. Figure 2 shows a homogeneous morphology of the produced nanocomposites characterized by spherulitic structures with an average diameter of ~1 μm.

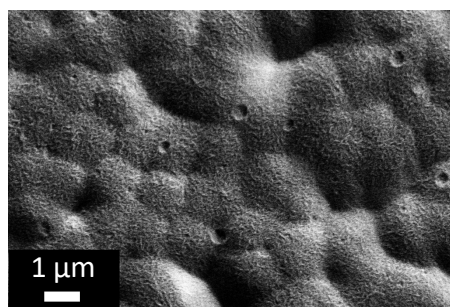


Figure 2 FE-SEM image of PVDF-TrFE loaded with 5 wt.% of CoFe₂O₄.

2.3. FT-IR Characterization

FT-IR analysis was performed over five different samples in order to understand if the β -phase fraction was influenced by the presence of the CoFe_2O_4 nanoparticles and by the successive magnetic poling. The FT-IR spectra of the nanocomposite specimens produced with a 5 wt.% of CoFe_2O_4 nanoparticles poled at two different intensities of DC magnetic field: 50 mT and 110 mT and with to different time: 60 min. and 120 min., are reported in Figure 3.

The relative fraction of the β phase, $F(\beta)$ can be evaluated, as reported in [1]–[3], [5], [6], [19], using the well-known equation:

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

where A_α and A_β are the absorbance at the wavelengths (763 and 840 cm^{-1}) associated to the main peaks of the α - and β -phases, respectively. The ratio between the absorption coefficients of the β - and α -phases is $K_\beta / K_\alpha \sim 1.3$.

As it can be observed the spectra of neat PVDF-TrFE presented two clear peaks at 763 cm^{-1} and 840 cm^{-1} that can be used to estimate the $F(\beta)$. From the data reported in Figure 3 we obtained a $F(\beta)$ value equal to 81.06 %, a value higher than the value obtained for pure PVDF [3] and in agreement with values reported for PVDF-TrFE in [20]. However, as reported in [17], when CoFe_2O_4 nanoparticles are added to the PVDF-TrFE, the FT-IR spectra show a broadband shoulder close to the α -phase peak located at 763 cm^{-1} , making difficult the evaluation of the relative fraction of β -phase by using eq. 1. We believe that the presence of this shoulder is due to the interaction between the polymer and the nanoparticles. This hypothesis was supported by the presence of a broad peak at 1740 cm^{-1} in the spectra of all PVDF-TrFE/ CoFe_2O_4 nanocomposite samples, which, as reported in [21], can be attributed to carbonyl groups (C=O). We speculate that this absorption band originates from the formation of bonds between O atoms of the CoFe_2O_4 nanoparticles and C atoms of PVDF-TrFE.

Nevertheless, as reported in [17], deconvolution of the shoulder from the absorption band related to the α -phase centered at 763 cm^{-1} , led an estimation of $F(\beta) = (82 \pm 3) \%$ for the different samples. This estimation and the observation that the intensity of the β -peaks remains unaffected by the introduction of CoFe_2O_4 nanoparticles as well as by the successive magnetic poling processes, provided evidences that the relative fraction of the β -phase remains nearly constant upon the introduction of the nanoparticles and is unaffected by the magnetic poling.

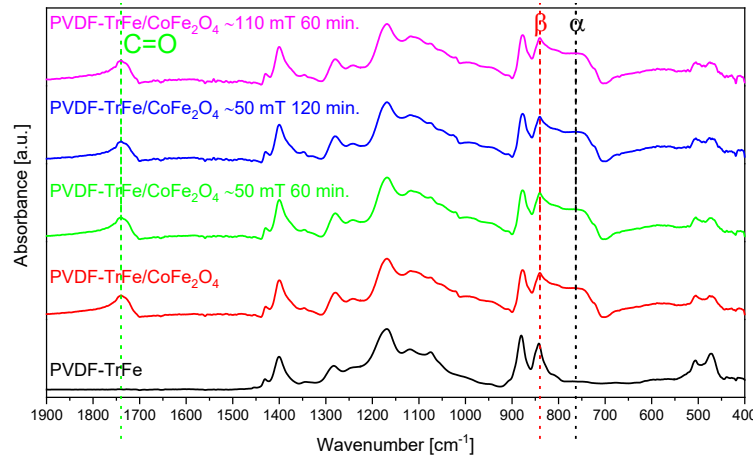


Figure 3 FT-IR spectra of the produced samples: i) neat PVDF-TrFE; ii) PVDF-TrFE filled with CoFe_2O_4 nanoparticles at 5 wt.%; iii) the PVDF-TrFE filled with CoFe_2O_4 at 5 wt.% and poled for 60 min. with a magnetic field of 50 mT; iv) the PVDF-TrFE filled with CoFe_2O_4 at 5 wt.% and poled for 120 min. with a magnetic field of 50 mT; v) the PVDF-TrFE filled with the CoFe_2O_4 at 5 wt.% and poled for 60 min with a magnetic field of 110 mT.

2.4. PFM Characterization

The piezoelectric properties of the PVDF-TrFE/CoFe₂O₄ nanocomposites were quantitatively evaluated by PFM measurements. An average piezoelectric coefficient (d_{33}) is determined by measuring three different regions of each sample and using the procedure developed in our previous works [2], [3], [22]. In Figure 4 were reported the d_{33} values for different applied DC magnetic field intensities, ranging from 0 mT to 220 mT. As can be seen, the piezoelectric coefficient increases when the magnetic field is increased and reaches a maximum value of (18.31 ± 1.06) pm/V for 1 h of the application of the magnetic field at 50 mT. Also shown in Figure 4 is the d_{33} value of a sample magnetically poled with a field of 50 mT at room temperature (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 have also investigated the effect of the application time of the DC magnetic field on d_{33} . Figure 4 (b) 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/CoFe₂O₄ nanocomposites particularly attractive for applications where electrical poling may have limitations.

We interpret the d_{33} increase induced by DC magnetic poling as 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 [23]. In particular, as suggested by the FT-IR analysis, we speculate that the formation of a carbonyl group (C=O) is related to the chemical bonding that can take place between PVDF-TrFE and CoFe₂O₄ nanoparticles. The application of the DC magnetic field induce the ferromagnetic nanoparticles to orient themselves along the direction of the applied field, dragging the polymeric chains of PVDF-TrFE in the same direction. As also reported in [23], we observed that the d_{33} reaches a maximum value when a relatively high magnetic field strengths is applied ($B \sim 50$ mT). Application of higher magnetic fields up to 220 mT produced a decrease in the d_{33} values after magnetic poling. As already pointed out, 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 (see Figure 4). This indicates that also the temperature plays a relevant role in the orientation of the β phase. Indeed, by increasing the temperature the polymeric nanocomposite becomes softer, facilitating the orientation of β phase along the applied magnetic field direction [17].

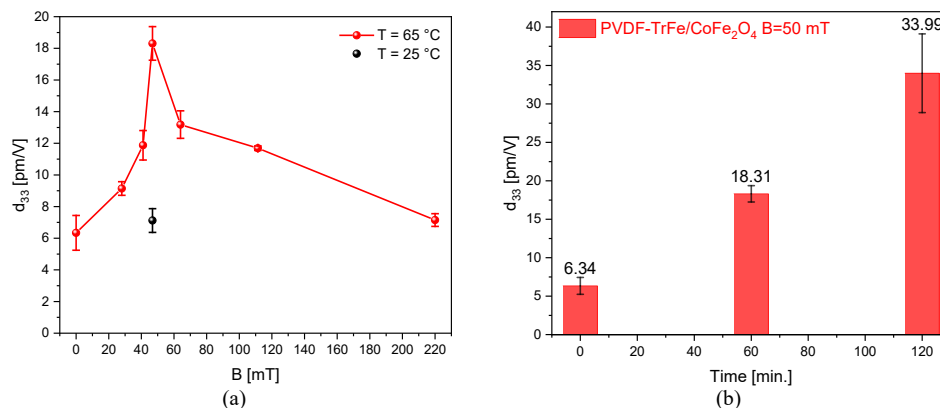


Figure 4 (a) d_{33} value of polymeric nanocomposites as a function of the amplitude of the applied DC magnetic field. The black point represents the value of d_{33} when the DC magnetic poling was performed at RT; (b) value of d_{33} of the nanocomposites with 5 wt % of CoFe₂O₄ as a function of the application time of the DC magnetic field.

2.4. Electromechanical Characterization

The optimized PVDF-TrFE/CoFe₂O₄ nanocomposites were used as active layers to fabricate flexible nanogenerators, using as top electrode a multilayer-graphene gold paper. In Figure 5 the response of the flexible

nanogenerators, based on PVDF-TrFE/CoFe₂O₄ nanocomposites poled with 50 mT for 1h and for 2h, are reported when a sinusoidal force of 0.25 N at the frequency of 110 Hz was applied through a commercial mini-shaker. A method similar to the normal load [24], [25] was used to estimate the piezoelectric coefficient d_{33} . We calculated the current collected from a RC circuit using an external resistance of 1 M Ω :

$$d_{33} = \frac{V_{out}}{2\pi f R |F|} \quad (2)$$

where V_{out} is the amplitude of the voltage acquired by a digital oscilloscope, R is the value of the load resistor and F is the magnitude of the applied force. A value of 19 pm/V and of 34 pm/V were evaluated, for the samples poled with 50 mT for 1h and for 2h, respectively. These values are in good agreement with the values (18.31 \pm 1.06) pm/V and (33.99 \pm 5.12) pm/V measured through PFM on the PVDF-TrFE/CoFe₂O₄ films before depositing the top electrode.

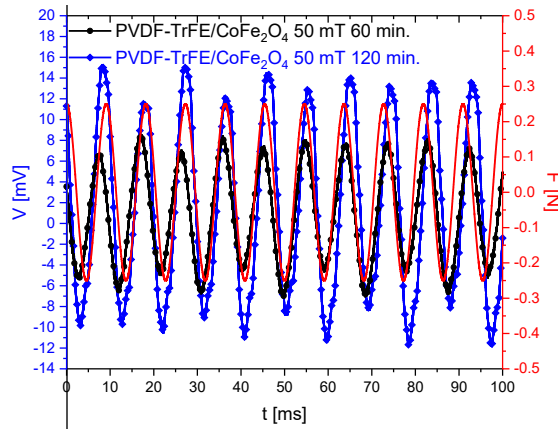


Figure 5 Electromechanical response of the PVDF-TrFE/CoFe₂O₄, poled with 50 mT for 1 h and 2 h (black and blue curve, respectively) when a load of 0.25 N at 110Hz was applied (red curve).

From the data reported in Fig. 5 we have then evaluated the power density:

$$PD = \frac{P}{A * t} \quad (3)$$

where A is the area solicited by our shaker (0.53 cm²), t is the thickness of our films (around 10 μ m) and $P = V^2/R$ is the power across the external resistance. As can be observed in Figure 6, we obtained an average value of 0.04 μ W/cm³ and of 0.136 μ W/cm³ for the samples poled with 50 mT for 1h and for 2h, respectively.

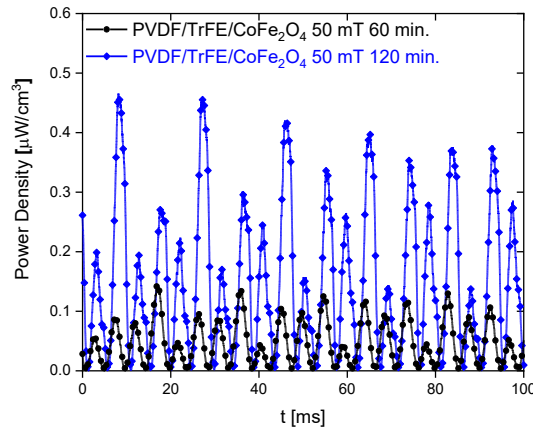


Figure 6 Calculated output power density across the external resistance for the sample poled with 50 mT for 1h (black line) and for 2h (blue line).

4. Conclusion

In this work we demonstrated flexible nanogenerators based on a high d_{33} piezoelectric polymeric nanocomposites, formed by adding ferromagnetic CoFe_2O_4 nanoparticles to PVDF-TrFE and performing a DC magnetic poling. The d_{33} value (34 pm/V) was obtained introducing 5 wt% of CoFe_2O_4 nanoparticles and applying a DC magnetic field of 50 for 2 h. Furthermore, we adopted an innovative solution to fabricate a flexible top electrode based on multilayer-graphene/gold paper. As confirmed by the appearance of the absorbance band at 1740 cm^{-1} in the FT-IR spectrum, the CoFe_2O_4 nanoparticles appear to be anchored to the PVDF-TrFE polymer chains through the formation of C=O bonds. We, then, believe that the increase of the d_{33} is due to the strong interaction between the CoFe_2O_4 nanoparticles and the magnetic field and their dragging effect over the polymeric chains of the PVDF-TrFE, resulting in their alignment along the direction of the applied DC magnetic field.

According to the analysis of the FT-IR measurements of the PVDF-TrFE/ CoFe_2O_4 nanocomposites, the intensity of the β -peaks remain nearly unaffected by the introduction of CoFe_2O_4 nanoparticles as well as by the successive magnetic poling processes. As a result, we can infer that the primary effect of the DC magnetic poling is to increase the orientation of the β -phase domains along the magnetic field direction, since the β -phase content remains nearly constant.

The developed combination of polymeric nanocomposite, including ferromagnetic CoFe_2O_4 nanoparticles, and the application of a DC magnetic poling provides an alternative route to obtain highly efficient piezoelectric materials with excellent d_{33} values. In particular, the magnetic poling appears to be easily implemented industrially, if compared to electrical poling, requiring the formation of top and bottom electrodes and the individual poling of each device. The electromechanical measurements have demonstrated how the produced device can be particularly attractive in the fabrication of energy harvesting devices for wearable sensors in flexible electronics applications. In particular, we observed that from the fabricated prototype we are able to extract a maximum power density of $0.438\text{ }\mu\text{W}/\text{cm}^3$.

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