

PFM Characterization of PVDF Nanocomposite Films With Enhanced Piezoelectric Response

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Abstract—The piezoelectric properties of PVDF mainly depend on its β phase. In this paper, we investigated through piezoresponse force microscopy the piezoelectric properties of PVDF composite films when we induce the formation of β -phase crystals adding a nanofiller, like graphene nanoplatelets or zinc-oxide nanorods, but without applying any electrical poling. At first, we fabricated piezoelectric PVDF nanocomposite films by the solution casting method. Then, we investigated the piezoelectric response of the different samples produced and we investigated the correlation between piezoresponse, morphology and structural characteristics of the nanocomposite. The morphology of the produced samples was investigated through field-emission scanning electron microscopy and atomic force microscopy. The β -phase formation was assessed through Fourier transform infrared spectroscopy measurements.

Index Terms—Nanofiller, PVDF, graphene nanoplatelets (GNPs), zinc oxide nanorods (ZnO-NRs), electroactive phase, piezoresponse force microscopy (PFM), piezoelectric coefficient (d_{33}).

I. INTRODUCTION

POLY(vinylidene fluoride) [PVDF; $(\text{CH}_2\text{CF}_2)_n$] is a semi-crystalline and ferroelectric polymer. Due to its chemical resistance, thermal stability, high mechanical strength, large remnant polarization, short switching time, and unique electrical properties, PVDF has attracted, in recent years, attention for its emerging application in organic electronics, biomedicine, optoelectronics and energy harvesters [1], [2]. In PVDF the amorphous and crystalline phases coexist. Several crystalline phases can be identified in PVDF (α -, β -, γ -, and δ -phase). The α -phase is non-polar and it is the most stable one when prepared by cooling from the melt. The β -phase exhibits the strongest ferro-, piezo-, pyroelectric properties, due to its largest

spontaneous polarization (7×10^{-30} cm) [3]. This phase is generally obtained through uniaxial or biaxial stretching of melt-crystallized films [4], melt crystallization under high pressure [5], crystallization from solution under special condition [6] or through the application of high electric fields to PVDF in its α -phase [7]. Depending on the processing route, β -PVDF can be obtained in a porous or non-porous form [8]. Several studies have also demonstrated that the addition of modified carbon nanotubes (CNTs) [9], modified graphene nanoplatelets (GNPs) [10], [11] or clay particles can induce β -phase formation in PVDF nanocomposites obtained by solution casting.

The aim of the present work is to investigate the piezoelectric properties of PVDF nanocomposite films through Piezoresponse Force Microscopy (PFM) and to correlate the piezoelectric response of the samples produced with the induced β -phase as revealed through Fourier transform infrared spectroscopy (FT-IR) measurements. In particular, we analyse whether an enhanced piezoresponse (i.e., d_{33} coefficient) is associated to an increase of the β -phase induced through the addition to the polymer of a nanofiller, like GNPs or zinc-oxide nanorods (ZnO-NRs), by means of two different production routes.

PFM is a very effective technique to characterize the piezoelectric properties of the materials at the nanoscale. PFM is able to study the local sample strain given by the applied electric field with a lateral resolution of a few nanometers [12], [13]. PFM is a versatile and non-invasive method to investigate the piezoelectric response of the ferroelectric material without an elaborate sample preparation.

The morphology of the produced samples was investigated through high-resolution field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM).

II. EXPERIMENTAL

A. Materials

PVDF (Solef 6010, Solvay Specialty Polymers, having molecular weight of 300,000–330,000 g/mol) was used as received. GNPs were produced by thermal expansion at 1150 °C for 5 s of a commercially available Graphite Intercalation Compound (GIC), and successive liquid-phase exfoliation by probe sonication, whereas ZnO-NRs were synthesized through thermal decomposition of zinc acetate di-hydrate, according to the procedure described in our earlier works [14]–[16]. N,N

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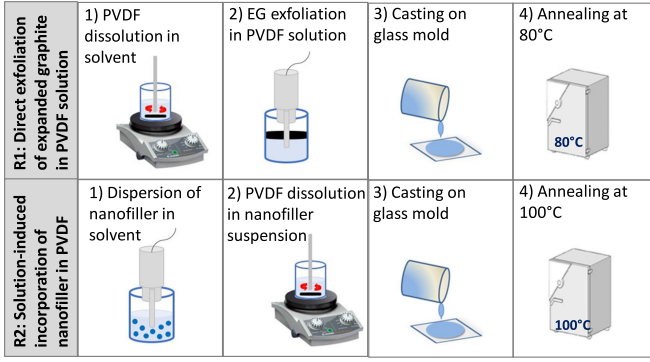


Fig. 1. Preparation routes of the PVDF nanocomposite film. After the evaporation of the solvent the self-standing film is peeled off the substrate.

dimethylformamide (DMF, Sigma–Aldrich, $\geq 99\%$) and acetone (ACS reagent, $\geq 99.5\%$) were employed as solvents.

B. Production of PVDF Nanocomposite Films

Two different production routes of PVDF nanocomposite films have been developed in order to enhance the piezoelectric response without the need for electrical poling, as sketched in Fig. 1.

1) *Route 1 (R1)—Direct Exfoliation of Expanded Graphite in PVDF Solution:* The GNP-PVDF nanocomposite films were fabricated via a solution mixing method [17]. PVDF was firstly dissolved in N,N-dimethylformamide (DMF), through 2 hours-magnetic stirring at 65 °C. Then, thermally expanded graphite (EG), produced through thermal expansion of a graphite intercalation compound (GIC) in air at 1150 °C for ~ 5 s [14], were dispersed in the PVDF-DMF solution using an ultrasonic processor in pulsed mode for 20 minutes. The obtained mixture was casted onto a glass plate and the solvent was evaporated in oven for 8 hours at 80 °C, as sketched in Fig. 1, R1. The weight concentration of the produced GNP-PVDF nanocomposite films were 0.3 wt%, 0.5 wt%, and 0.7 wt%. Once produced the obtained films, having thickness of approximately 30 μm , were peeled off the substrate. According to our previous research works [17], [18], the advantage of this method is that, at concentrations below 1 wt%, nanostructures are dispersed homogeneously inside the polymer matrix. Moreover, GNPs are distributed uniformly amongst polymer chains by this method. This results in enhancement of the β -phase in PVDF nanocomposites.

Neat PVDF film was fabricated following only steps 1, 3, 4 in Fig. 1, R1.

2) *Route 2 (R2)—Solution-Induced Incorporation of Nanofiller in PVDF:* PVDF nanocomposites films loaded with a low amount of nanofillers (0.1 wt%) were prepared through solution-induced incorporation of the nanofiller in the polymer [18].

At first, nanofillers (either GNPs or ZnO-NRs) were dispersed homogeneously in a solvent mixture through a short probe sonication cycle (5 min in pulse mode at 40% in power amplitude). Next, PVDF powder was added to the as-obtained nanofiller

TABLE I
LIST OF PVDF FILMS PREPARED, THEIR COMPOSITION AND PRODUCTION PROCESS

Sample	Preparation Route	GNPs (wt.%)	ZnO-NRs (wt.%)
R1-PVDF	R1	-	-
R1-GNP-0.3	R1	0.3	-
R1-GNP-0.5	R1	0.5	-
R1-GNP-0.7	R1	0.7	-
R2-PVDF	R2	-	-
R2-GNP	R2	0.1	-
R2-ZnO	R2	-	0.1

suspension and stirred for 3 h. Flexible and self-standing films, having thickness of approximately 15 μm , were obtained by casting the nano-filled solution onto a clean glass plate, followed by subsequent solvent evaporation in an oven at 100 °C for 12 h, as sketched in Fig. 1, R2.

Neat PVDF was prepared by dissolving PVDF powder in a mixture of DMF and acetone (1:1 v/v). A clear and transparent solution was obtained upon continuous stirring at room temperature for 3 h, ensuring the complete dissolution of PVDF. The solution was casted onto a clean glass plate and subsequently placed in an oven at 100 °C for 12 h for the complete evaporation of the solvent.

All produced samples and related preparation method are summarized in Table I.

B. Morphological and Structural Characterizations

The morphology of the produced samples was observed using Field Emission Scanning Electron Microscopy (FE-SEM, Zeiss Auriga) operated at an accelerating voltage of 5 kV. Before SEM imaging, the produced samples were coated with a thin homogenous 20 nm Cr layer, using a sputter coater (Quorum Q150T ES).

The FT-IR system was a single-beam instrument (Bruker Tensor 27), equipped with a room temperature deuterated triglycine sulfate (DTGS) detector, mid-IR source and a KBr beamsplitter. Spectra were acquired in the range 4000–600 cm^{-1} with resolution of cm^{-1} . Samples were analyzed in the attenuated total reflection (ATR) configuration, using the Pike Miracle ATR cell equipped with a Diamond/ZnSe crystal, with a sampling area of 6 mm diameter.

D. Piezoresponse Force Microscopy (PFM)

PFM measurements were performed using a commercial Bruker-Veeco Dimension Icon AFM, equipped with the piezoelectric module under the following conditions: silicon cantilever (Bruker) with 115–135 μm length, nominal spring constant of 5 N/m, Co-Cr coated tip with electrical resistivity of 0.01–0.025 $\Omega\cdot\text{cm}$, tip curvature radius 35 nm and nominal resonance frequency of 150 kHz. In order to measure the

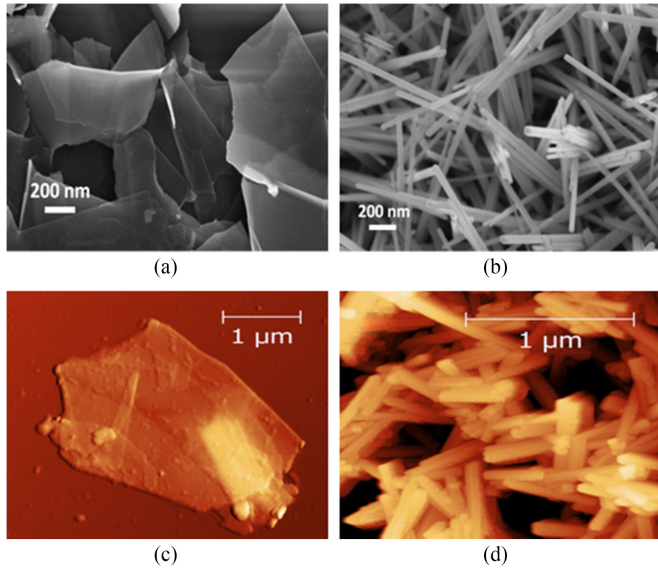


Fig. 2. FE-SEM micrographs of (a) GNPs, and (b) ZnO-NRs. AFM micrographs of a (c) GNP flake, and (d) ZnO-NRs.

piezoresponse of the samples, an a.c. voltage was applied to the tip, with amplitude varying from 0 V to 10 V at a fixed frequency of 15 kHz. Scan rate was 0.5 Hz and the scan area was $(500 \times 500) \text{ nm}^2$. The dimension of the scan area was selected considering that the PVDF films have a porosity in the range of tens of microns. The scope is to perform a local characterization of the piezoelectric response of the material, avoiding that the topography signal interferes with the PFM measurement. Ten different areas were scanned for each sample and the measured data were averaged. All measurements were performed in an insulating chamber to avoid acoustic excitation.

III. RESULTS AND DISCUSSIONS

A. Morphology

Fig. 2 shows FE-SEM and AFM images of GNPs and ZnO-NRs used in this study as fillers. It is observed that GNPs are characterized by thickness in the range of 2–10 nm and average lateral dimensions of up to a few microns, whereas ZnO-NRs have average diameter in the range 30–40 nm and length of $\sim 500 \text{ nm}$.

FE-SEM image of neat PVDF produced according to route 1 are shown in Fig. 3(a)–(h). The surface is characterized by spherulitic structure with porosity in the micrometric range. Upon addition of GNPs, we observed a similar spherulitic structure, and a good integration between GNPs and the polymer matrix, since GNPs are well embedded into the PVDF. Fig. 3(d), (f), and (h) show detailed views of GNPs emerging from the surface of the composite films and partially covered by the polymer matrix at 0.3 wt%, at 0.5 wt% and at 0.7 wt%, respectively.

We observed that the dimensions of the spherulites decrease as the GNP concentration increases, as described in [17]. The average values of the spherulite diameter, estimated from the FE-SEM images, are reported in Table II.

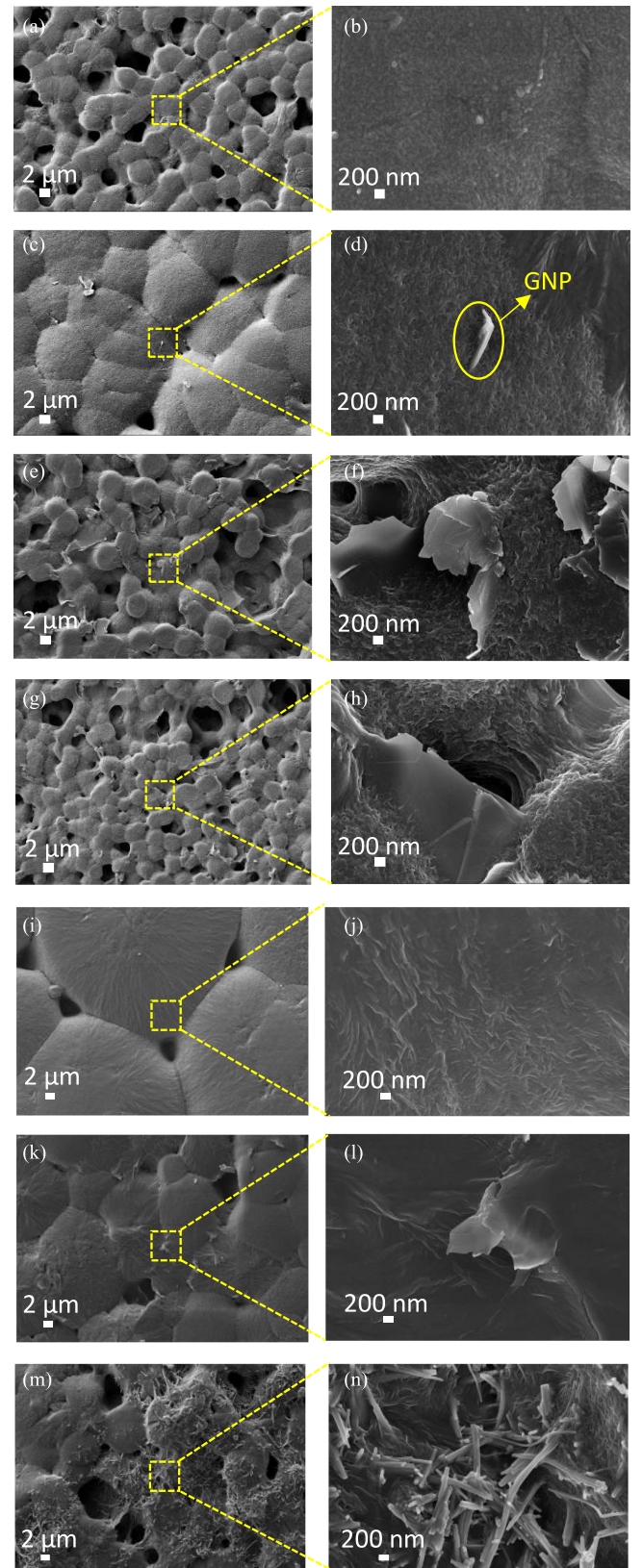


Fig. 3. FE-SEM image of PVDF films produced. Via route 1: neat PVDF (a), (b) PVDF-GNP nanocomposite at 0.3 wt% (c), (d), PVDF-GNP nanocomposite at 0.5 wt% (e), (f), PVDF-GNP nanocomposite at 0.7 wt% (g), (h). Via route 2: neat PVDF (i), (j), PVDF-GNP nanocomposite at 0.1 wt% (k), (l), PVDF-ZnO-NR nanocomposite at 0.1 wt% (m), (n).

TABLE II
AVERAGE VALUES OF THE SPHERULITE DIAMETER ESTIMATED
FROM FE-SEM IMAGES

Sample	Spherulite diameter (μm)
R1-PVDF	4.87 ± 0.97
R1-GNP-0.3	9.79 ± 2.31
R1-GNP-0.5	5.00 ± 0.95
R1-GNP-0.7	4.13 ± 0.20
R2-PVDF	28.58 ± 4.56
R2-GNP	13.47 ± 4.09
R2-ZnO	7.25 ± 1.40

FE-SEM images of PVDF-nanocomposite films produced through routes R2 are shown in Fig. 3(i)–(n). It is evident that the solution mixing leads to a homogenous dispersion of the 2D shaped GNPs and of the rod-shaped ZnO-NRs in the PVDF matrix, due to the respective interaction of carboxyl and hydroxyl groups of nanofillers with PVDF [19]. Nanofillers are well encapsulated within the polymer matrix, thereby resulting in a good interfacial interaction. This interaction changes the morphology of the polymer surrounding the nanostructures, as can be observed through the comparison of the micrographs in Fig. 3(l), (n), and (j), the latter representing the neat PVDF sample. In general, it is observed that the average larger spherulites are found in all samples produced according to route 2. This is probably due to the fact that the EG exfoliation in the PVDF solution through ultrasonication produced a disruption of the polymer chains.

B. FT-IR Analysis

The presence of the β -phase in the produced PVDF nanocomposite films was assessed using FT-IR spectroscopy. The characteristic peaks attributed to the FT-IR absorbance band of α -phase are located at 1423, 1383, 120, 1147, 976, 855, 795 and 763 cm^{-1} [16]. The electroactive polar β -phase can be well identified from peaks at 1275 cm^{-1} and 840 cm^{-1} , whereas the semi-polar γ -phase is evident from the peak at 1234 cm^{-1} [20], [21].

All samples produced according to the different routes R1–R2 showed the presence of the electroactive phase, evinced through the characteristic γ peak at 1234 cm^{-1} and β peak at 840 cm^{-1} , as shown in Fig. 4.

FT-IR measurements are used to evaluate the fraction of the electroactive β -phase of PVDF, by using the following equation [22]:

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

where $F(\beta)$, represents the β -phase content; A_α and A_β are the absorbance at 766 and 840 cm^{-1} ; being K_α and K_β the absorption coefficients at the corresponding wavenumbers, whose

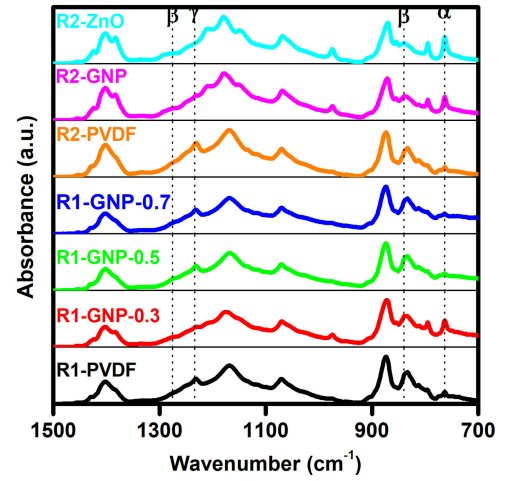


Fig. 4. FT-IR spectra for PVDF nanocomposite films produced through route 1 and route 2.

TABLE III
RELATIVE FRACTION OF THE β -PHASE ESTIMATED FROM FT-IR SPECTRA $F(\beta)$ AND PIEZOELECTRIC COEFFICIENT d_{33} EVALUATED BY AVERAGING THE PFM SIGNAL OVER 3 MEASUREMENT AREAS, (500 $\times$ 500) nm^2 IN SIZE

Sample	$F(\beta)$	d_{33} (pm/V)
R1-PVDF	0.687	2.24 ± 0.75
R1-GNP-0.3	0.481	3.18 ± 1.46
R1-GNP-0.5	0.647	5.19 ± 1.49
R1-GNP-0.7	0.615	3.95 ± 1.33
R2-PVDF	0.694	4.38 ± 1.60
R2-GNP	0.455	6.16 ± 1.00
R2-ZnO	0.380	6.08 ± 1.53

values are 6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, respectively. The obtained values are reported in Table III.

We notice that in GNP-PVDF nanocomposite films produced according to R1, the fraction $F(\beta)$ is not directly proportional to the amount of GNP content. This is due to the fact that as shown in Fig. 3 and reported in Table I, the morphology and spherulite size of these composites are quite different. In PVDF nanocomposite films produced according to routes R2, we noticed that when we added the nanofiller the fraction of the β -phase increases.

C. Piezoelectric Properties

In order to evaluate the piezoelectric properties of our samples we estimated the piezoelectric coefficient d_{33} through PFM. This technique is based on the standard contact mode AFM setup, in which the cantilever and the tip are electrically conductive and an alternating voltage is applied to the tip [13].

The measured amplitude signal is converted into a displacement amplitude signal by applying a calibration factor, which is obtained through the measurement of a well-known piezoelectric material. To this purpose, in our study, a Bruker reference sample, consisting of a periodically poled lithium niobate (PPLN) specimen, with an effective piezoelectric coefficient

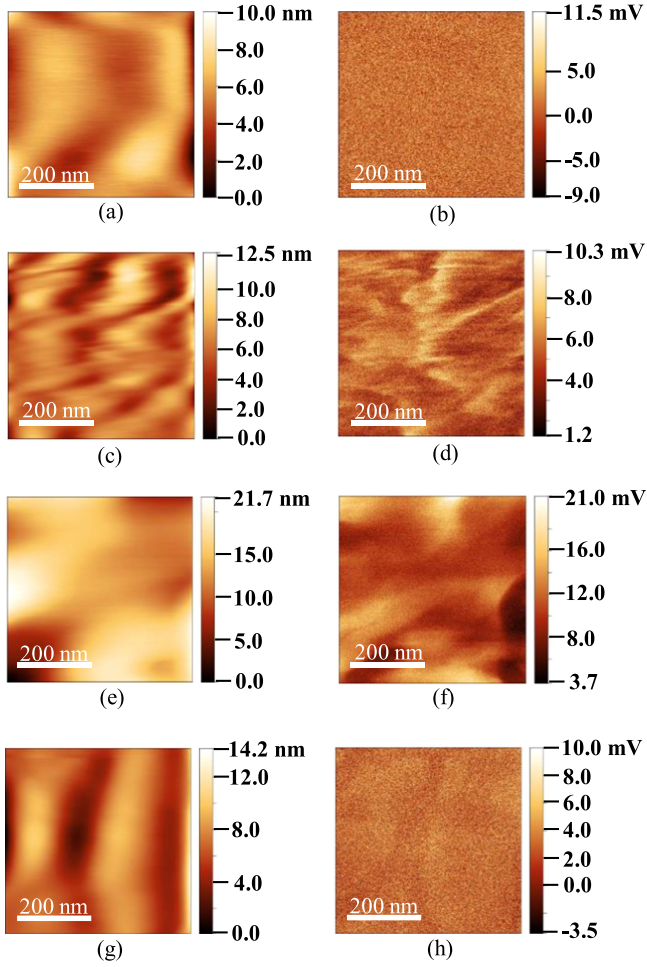


Fig. 5. Topography map of (a) neat PVDF, (c) PVDF/GNP at 0.3 wt%, (e) PVDF/GNP at 0.5 wt% and (g) PVDF/GNP at 0.7 wt%, domain contrast of PFM for (b) neat PVDF, (d) PVDF/GNP at 0.3 wt%, (f) PVDF/GNP at 0.5 wt% and (h) PVDF/GNP at 0.7 wt% at 10 V.

$d_{33-PPLN} = 7.5 \text{ pm/V}$, was employed. In the ideal case the amplitude of the measured piezoresponse A_{piezo} is given by:

$$A_{piezo} = \xi d_{33} V_{ac} \quad (2)$$

in which ξ is a calibration parameter, d_{33} is the effective piezoelectric coefficient measured via PFM and V_{ac} is the alternating voltage.

At first, we measured the piezoelectric response of the calibration sample and we estimated the slope m_{PPLN} of the linear fitting of the piezoresponse amplitude versus the applied voltage. Then, we estimated the calibration factor as:

$$\alpha = m_{PPLN}/d_{33-PPLN} \quad (3)$$

in which $d_{33-PPLN}$ is the known piezoelectric coefficient of the reference sample. Finally, we measured the response of the sample under test and we estimated its d_{33} from (2), using the calculated calibration factor ξ . In the considered test setup, we applied an a.c. voltage to the sample under test, through the tip, while grounding the bottom electrode.

In Fig. 5 AFM height and piezoelectric contrast signals, over a scanning an area of $(500 \times 500) \text{ nm}^2$, are reported.

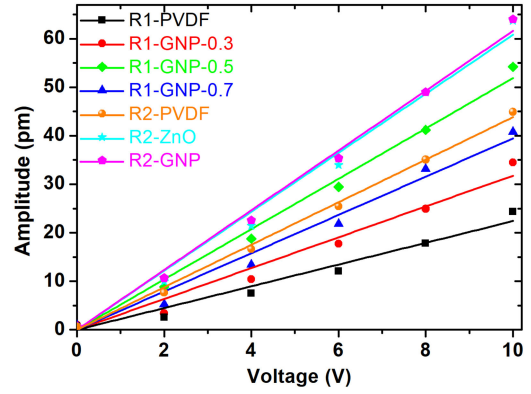


Fig. 6. Measured piezoelectric signal, averaged over the 19 areas, versus the amplitude of the applied a.c. voltage.

From the reported micrographs it is clear the lack of a direct correlation between the piezoelectric contrast and the topography, indicating that the β -phase domains are not related to the morphology of the films [23]. Therefore, we can say that the piezoelectric effect is due to intrinsic piezoelectric properties of the materials and not originated from the cross-talk with the topography. This is in agreement with the results reported in PVDF by Serrado Nunes *et al.* [23], showing that the piezoelectric constant does not directly follow the topographic shape.

In order to evaluate the average piezoelectric properties of the samples we performed PFM measurements on 10 different regions for each sample (scanning area $(500 \times 500) \text{ nm}^2$). In Fig. 6 we report the average values of displacement, obtained from all measurements, as a function of the amplitude of the applied a.c. voltage.

We noticed that, when we added the nanofillers through route 1, the presence of the β -phase, as revealed via FT-IR analysis is not directly correlated to a high value of the piezoresponse coefficient. On the contrary, when we added the nanofillers through route 2, we observed a significant enhancement of d_{33} , as compared to the value estimated for the neat PVDF, although the low content of the β -phase revealed via FT-IR analysis.

In order to correlate the piezoelectric coefficient with the presence of the β -phase in the samples, we reported d_{33} vs $F(\beta)$ in Fig. 7 for all produced samples.

As can be observed in Fig. 7, for both routes R1 and R2, the piezoelectric coefficient of PVDF nanocomposite films increases upon addition of the nanofillers, as compared to neat PVDF (R1-PVDF and R2-PVDF). In particular, for samples produced via route 1 (R1-GNP-0.3, R1-GNP-0.5 and R1-GNP-0.7) the increase in the piezoelectric coefficient is generally proportional to the fraction of β -phase. A different behavior is observed when we added nanofillers following route 2 (sample R2-GNP and R2-ZnO): although FT-IR data show a low amount of the β -phase, we observed an enhancement of d_{33} , as compared to neat PVDF (R2-PVDF). In particular, we observed that the highest values of d_{33} have been obtained adding the nanofillers using route 2, despite the lower content of β -phase, as compared to samples obtained using route 1. A possible explanation for such behavior, can be ascribed to the different

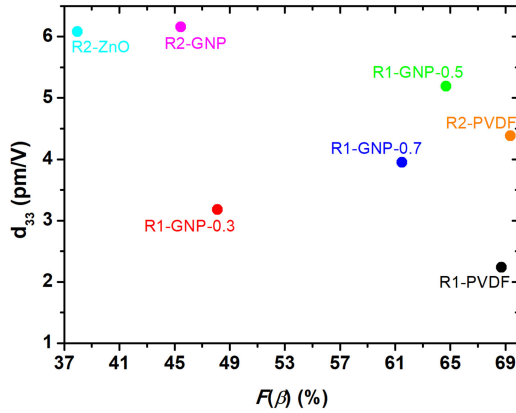


Fig. 7. Averaged piezoelectric coefficient, d_{33} vs the relative fraction of the β -phase, $F(\beta)$.

TABLE IV
QUANTITATIVE COMPARISON BETWEEN OUR BEST VALUE OF d_{33} AND
THE RECENTLY LITERATURES RESULTS

Sample	d_{33} (pm/V)	Ref.
This work	~6	
PVDF+MWCNT	~4	[24]
Theoretical PVDF+Gr	~12	[25]
PVDF+montmorillonite	~7	[26]

fabrication processes employed. In fact, in route 1 we used a tip-sonication to disperse the GNPs directly into the polymer solution. Whilst such process guarantees a good dispersion and uniformity of the filler in the polymer matrix, it also induces defects and damages to the polymeric chains, resulting in a lower d_{33} , if compared with samples produced through route 2, where the absence of a direct tip-sonication on the polymer solution, ensures the integrity of the polymeric chains.

We note that the values of d_{33} for PVDF nanocomposites investigated in this work are comparable with those reported for undrawn and poled PVDF films filled with multiwalled carbon nanotubes (MWCNT) [24], with PVDF films filled with graphene/graphene oxide [25] and PVDF filled with montmorillonite [26]. In Table IV we report a quantitative comparison between our best value of d_{33} and the recent literature. We notice that the highest value of d_{33} expected for non-poled PVDF, according to theoretical calculations, is 12 pm/V [25]. On the other hand the experimentally measured d_{33} values are normally lower than the theoretical values and are in the range of 3–7 pm/V [24], [26]. This confirms that our PVDF nanocomposites have a promising piezoelectric response, as they can provide similar d_{33} values, though without the need for any poling step.

IV. CONCLUSION

We presented a novel approach to increase the piezoelectric coefficient of PVDF, avoiding the poling process, by inducing an increased β -phase fraction in the PVDF film through the addition of suitable quantities of nanofillers. Using a simple casting process we produced free standing flexible PVDF

nanocomposite films. Two different routes have been investigated to induce an enhancement of the piezoelectric response of PVDF. Seven different samples have been produced: neat PVDF (R1-PVDF and R2-PVDF), PVDF nanocomposites filled with GNP at 0.1 wt% (R2-GNP), 0.3 wt% (R1-GNP-0.3), 0.5 wt% (R1-GNP-0.7) and 0.7 wt% (R1-GNP-0.7) and with ZnO NRs at 0.1 wt% (R2-ZnO). The enhancement of the piezoelectric response of the nanocomposites can be explained by assuming that GNPs or ZnO NRs can influence the polymer structure arrangement, as to induce the β -phase formation in PVDF, as already reported in previous studies [16], [10], [17].

The results of this study show a qualitative correlation between induced β -phase, as assessed through FT-IR measurements, and intensity of the measured piezoelectric response, resulting from the PFM analysis. In fact, the obtained PFM data show the local value of the piezoelectric coefficient, measured over the sample surface over 10 spots having dimension of $(500 \times 500) \text{ nm}^2$. Therefore, the obtained results demonstrate the piezoelectric behavior of the nanocomposite films, induced by the presence of a β -phase, which is obtained without modification or functionalization of GNPs or ZnO NRs, nor through the application of any strain or electric field during the synthesis.

We obtained a higher value of d_{33} adding nanofillers using route 2, despite the concentration of β -phase was lower than the samples obtained using route 1. We speculate that this behavior can be correlated to the tip-sonication process, employed in route 1 to disperse GNPs, and that could lead to a reduction in the length of polymeric chains, resulting in a lower d_{33} .

The obtained results can be very attractive for the fabrication at low processing temperatures of energy harvesting devices or pressure sensors on flexible substrates, avoiding chemical modification or poling.

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