

Accepted for OA journal *Advanced Electronic Materials* 2023

Optimizing Piezoelectric Coefficient in PVDF Fibers: Key Strategies for Energy Harvesting and Smart Textiles

Sunija Sukumaran, Piotr K. Szewczyk, Joanna Knapczyk-Korczak, Urszula Stachewicz

Faculty of Metals Engineering and Industrial Computer Science, AGH University of Krakow,
30-059 Krakow, Poland

Keywords

PVDF, electrospun fiber, thermal annealing, reduced graphene oxide, piezoelectricity, crystallinity

Abstract

With the advancement in smart electronic devices and self-powered devices, the demand for piezoelectric polymers found potential research interest. Among these, electrospun polyvinylidene fluoride (PVDF) fibers have gained attention for energy harvesting due to their flexibility and higher piezoelectric coefficient. We compare various methods to enhance PVDF's piezoelectric properties, including different solvents (DMAc, DMF), conductive filler (rGO), and annealing as post-treatment. Our results indicate that PVDF/rGO fibers in DMAc solvent exhibit the highest β phase fraction and crystallinity. Moreover, for the first time, we present the piezoelectric properties of PVDF/rGO electrospun single fiber using high voltage switching spectroscopy piezoelectric force microscopy (HVSS-PFM). The highest piezoelectric coefficient (d_{33}) was measured for PVDF/DMAc-rGO composite fibers. Notably, PVDF/rGO in DMAc solvent significantly improves the piezoelectric coefficient, leading to a remarkable fourfold increase in power density compared to pure PVDF, making it a promising material for energy harvesting applications.

1. Introduction

The advances in lightweight, portable, and deformable electronic devices such as sensors, actuators, and various energy harvesters demand highly flexible electroactive materials^[1–3]. To date, mechanical energy is considered the extensively used renewable energy harvesting approach due to its vast availability everywhere^[4]. Hence, piezoelectric materials have found immense research attention due to their unique property of converting mechanical energy into electrical energy and vice-versa^[5]. Various piezoelectric materials such as lead zirconate titanate (PZT)^[6], barium titanate (BaTiO₃)^[7], zinc oxide (ZnO)^[8], gallium nitride (GaN)^[9], sodium potassium niobate (KNN)^[10] were used to generate energy. The relatively low piezoelectric power output from GaN and ZnO limits their practical applications as flexible energy harvesters^[10]. Several studies have been performed on PZT and its composites due to the highest piezoelectric coefficient of PZT (175 pC/N)^[6,11]. Though, employing toxic Pb-based piezoceramics poses a hazard to the environment as well as human health^[12]. Wu et al^[10], prepared a flexible lead-free PDMS composite film consisting of KNN piezoelectric particles with a composition of 0.91K_{0.48}Na_{0.52}NbO₃-0.04Bi_{0.5}Na_{0.5}ZrO₃-0.05AgSbO₃-0.2%Fe₂O₃ (KNN-BNZ-AS-FE). However, preparing the KNN-BNZ-AS-FE particles is quite complex and involves many steps. Also, the PDMS- KNN-BNZ-AS-FE film requires poling at the high electric field. Contrary to above mentioned piezoelectric materials, piezoelectric polymers possess many advantages, such as flexibility, lightness, high deformability, and easy fabrication^[11,13]. This makes them a suitable candidate for wearable, flexible, biomedical, and implantable electronic devices^[14,15]. However, the polymer's relatively low piezoelectric coefficient compared to ceramic materials limits their practical applications^[16].

Polyvinylidene fluoride (PVDF) and its copolymers found great research interest owing to its excellent piezoelectric, pyroelectric, and ferroelectric properties^[11]. Amongst the existing piezoelectric polymers, it has the highest piezoelectric coefficient and dielectric permittivity^[1,17]. The low cost, high flexibility, mechanical stability, low density, and biocompatibility of PVDF polymers further strengthen its applications in numerous fields, especially in energy harvesters, smart textiles, and small electronic devices^[18,19]. PVDF is a semicrystalline polymer and has different chain conformations in five crystalline phases, namely, α (TGTG'-trans-gauche-trans-gauche), β (TTT-all trans), δ (TGTG'), γ (T3GT3G')

and ϵ (T3GT3G')^[20]. The piezoelectric property of PVDF is caused by the intense electric dipole moment that occurs in the PVDF monomer. It is due to the higher electronegativity of fluorine atoms than hydrogen and carbon atoms. From the PVDF chain conformation, α and ϵ have zero dipole moment, though β , δ , and γ (electroactive phase) possess a net dipole moment. The highest dipole moment per unit cell belongs to the β phase, which is responsible for the piezoelectricity in PVDF^[20–22]. The non-polar α phase is mainly formed when PVDF is cooled from a melt form^[23]. An external polarization process or mechanical stretching increases PVDF's polar β phase content^[24]. Nevertheless, the polarization at a high electric field can cause electrical breakdown and structural damage^[25]. In this context, electrospinning is considered a facile and efficient technique for producing self-poled PVDF nano/microfibers^[26,27]. Through electrospinning, PVDF polymer with enhanced piezoelectric properties can be prepared by a single-step mechanical stretching and electrical poling process^[1,28]. Moreover, using this technique, it is possible to tune the surface morphology and properties of polymer fibers by controlling specific parameters such as applied voltage^[29], polymer^[30], temperature^[31], humidity^[32], solution feed rate and many more^[1,33]. The structural changes affect not only the piezoelectric properties but also the mechanical and surface properties^[34,35].

In addition to the electrospinning conditions, other factors, such as solvents, polymer concentration, molecular weight, solution conductivity, surface tension, and viscosity, significantly improve the β phase content and crystallinity of the PVDF electrospun fibers^[36,37]. The major impact on PVDF crystallinity and the piezo response was noticed with solvents, additions of fillers based on graphene oxide (GO) or ceramic nanoparticles, and postprocessing, such as annealing. Several studies have recently been published on the structural properties relationship between the effects of different solvents and electrospinning parameters on the morphology and crystallinity of PVDF electrospun fiber^[1,38,39]. The most commonly used solvent is DMF in most of the electrospun PVDF studies, ^[38,40]. Still, there is a literature gap on how the solvents affect PVDF's crystallinity, β phase content, and piezoelectric coefficient. Also, no comprehensive study was reported comparing the electrospinning of PVDF solution with dimethylacetamide (DMAc) and DMF solvents which are vastly used to produce PVDF fibers. Therefore, we carried out a detailed study on crystallinity, β phase content, and piezoelectric coefficient of PVDF single fibers and mats based on DMAc and DMF solvents.

100

101 Another widely used approach is incorporating fillers into the polymer matrix, which has the
 102 potential to remarkably enhance the physical properties of the polymer matrix^[41–43].
 103 Additionally, certain fillers such as carbon nanotubes (CNTs)^[44], nanoclays^[45], zinc oxide
 104 (ZnO)^[46], sodium potassium niobate (KNN)^[47], barium titanate (BaTiO₃)^[48], graphene and
 105 its derivatives^[49] induce an electroactive phase in the polymer matrix. Recently, graphene
 106 oxide (GO) and reduced graphene oxide (rGO) fillers have received significant research
 107 attention due to their high surface area and excellent mechanical and electrical
 108 properties^[50,51]. Aside from increasing the β -phase content, induced charge transfer directly
 109 impacts electrical power generation^[28,52]. Because of their high electrical conductivity, GO
 110 and rGO are used as conductive fillers, , allowing energy harvesting and conversion
 111 applications^[53,54]. Yang et al.^[52] compared the effects of GO and in-situ reduced rGO on
 112 PVDF electrospun nanofibers. The study demonstrates that the conductivity of rGO is more
 113 than four times higher than that of GO.

114

115 Post-treatment is another common practice to enhance the piezoelectric response of PVDF
 116 and its copolymers^[55,56]. Additional to mechanical stretching and electric polarization,
 117 thermal annealing is one of the effective methods to alter the phase transition, orientation of
 118 chains, and crystallinity of PVDF^[57,58]. Many studies were reported based on the effect of
 119 thermal treatment on the morphology, chain orientation, mechanical properties, and
 120 crystallinity of PVDF films^[58–61]. However, no comprehensive study has been reported based
 121 on the effect of annealing post-treatment on electrospun PVDF and composite and
 122 comparing the piezoelectric constant of individual fibers and bulk fiber mats.

123

124 So far, it has been proved that the abovementioned affect the piezoresponses of electrospun
 125 PVDF. Still, there is no comparison of which is the most effective strategy. Therefore, in
 126 this study, we aim to verify the effect of the two best solvents: DMAc and DMF, adding rGO
 127 to fibers and annealing as the post-treatment. Here we compare these strategies regarding β
 128 phase content, crystallinity, and piezoelectric constant of PVDF fibers. Furthermore, the
 129 first-time high voltage switching spectroscopy piezoelectric force microscopy (HVSS-
 130 PFM) results for individual fibers were compared with the piezoelectric coefficient of the
 131 fiber mat. In the current trends of smart textiles developments and their importance for

energy harvesting applications selecting the best way to produce high-piezoresponse PVDF fibers is crucial for enhancing energy generation performance and saving production costs.

2. Results and discussion

We produced randomly oriented PVDF and PVDF-rGO nanocomposite fibers using two solvents DMAc and DMF, via electrospinning. Comparing the synergistic effects of solvents, rGO filler, and the post-annealing treatment allowed us to control the piezoelectric coefficient. Therefore, it helps to choose the best method to prepare the PVDF mats on a large scale for smart textiles and energy harvesting applications. The schematic representation of the steps followed to prepare the PVDF/rGO composite is presented in Figure 1. Finally, all produced materials were analyzed based on their electroactive characteristics.

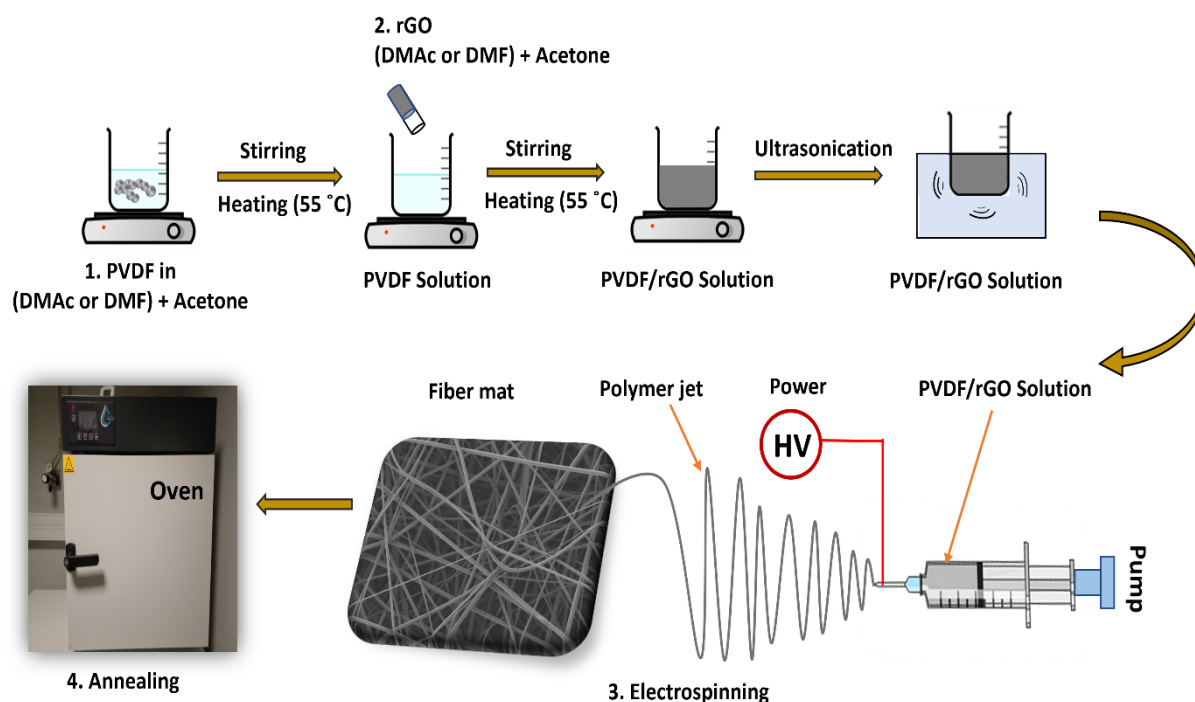


Figure 1. Schematic representation of the PVDF/rGO composite fibers preparation steps (1) PVDF solutions preparation in DMAc/Acetone and DMF/Acetone (2) PVDF/rGO solutions in DMAc/Acetone and DMF/Acetone (3) Electrospinning of the prepared solutions (4) Annealing of the fiber mats.

The SEM micrographs for all the PVDF fibers and composites are presented in the Supporting Information in Figure S1. We have obtained bead-free and uniform PVDF fibers by optimizing the electrospinning parameters shown in Table S1 in the Supporting

Information. From the fiber diameter distribution curve (Figure 2a and 2b), it can be observed that the average fiber diameter of the PVDF/DMAc was $1.39 \pm 0.4 \mu\text{m}$ which is less than the average fiber diameter of PVDF/DMF fibers ($1.63 \pm 0.4 \mu\text{m}$). The evaporation-stretching function can cause a difference in fiber diameter between the two electrospun membranes during electrospinning. Also, solution conductivity plays an important role in stretching the charged polymer jet in electrospinning^[62], which causes structural changes in deposited fibers^[63]. The conductivity measured for DMAc solvent was $0.300 \pm 0.013 \mu\text{Scm}^{-1}$, which is higher than the conductivity of DMF solvent $0.241 \pm 0.013 \mu\text{Scm}^{-1}$. The SEM and corresponding fiber diameter distribution curves of the annealed PVDF/DMAc and PVDF/DMF fibers revealed that the morphology of the annealed fiber membrane looks like the pristine PVDF fibers both in DMAc and DMF solvent. No noticeable morphological changes have occurred in the annealed fibers compared with pristine fibers. The annealing treatment could not significantly change the fiber diameter in aPVDF/DMAc or aPVDF/DMF fibers. Sathiyaraju et al.^[64] found similar results by annealing the PVDF fiber at different temperatures and observed no significant change in the morphology of fibers. Gee et al.^[65] performed optimization studies for PVDF nanofiber membranes with three different solvents, DMF, DMSO, and N-Methyl-2-pyrrolidone (NMP) and demonstrated that DMF/Acetone produced membrane had the smallest average fiber diameter compared to DMSO and NMP. Also, DMF/Acetone showed the highest β phase fraction among DMSO and NMP. However, there is no information regarding the relative humidity of electrospinning, which can vary fiber's morphology and chemical composition of surfaces^[26].

Yin et al.^[5] studied the effect of solvents (DMF, DMSO) and electrospinning parameters on the piezoelectric properties of PVDF polymer with an atmospheric environment of temperature $20 \pm 3 ^\circ\text{C}$ and humidity of $45 \pm 5\%$. Contrary to the results showed by Gee et al., Yin et al. presented that DMSO/Acetone solvent had a smooth surface and uniform shape of the nanofibers. However, DMF/Acetone solvent results in beaded nanofiber with various diameters and consistent morphology. The authors described that this is due to the higher conductivity of the DMSO/Acetone solvent. Also, they reported that the evaporation of the solvent effect has less effect on the fiber diameter than the conductivity of the solution. These agree with our results, though the boiling point is higher for DMAc than DMF. However, DMAc has higher solution conductivity and allows for obtaining a lower

fiber diameter. This confirms the more pronounced effect of conductivity on the process than the solvent evaporation during electrospinning.

Adding 1 wt% rGO to PVDF/DMAc and PVDF/DMF electrospun fibers results in a bead-free structure. See Figure S1 in the Supporting Information. Moreover, no volatilized solvents were found in the composite fibers. Furthermore, the fiber diameter of PVDF/DMAc-rGO and PVDF/DMF-rGO was $0.61 \pm 0.3 \mu\text{m}$ and $0.70 \pm 0.3 \mu\text{m}$, respectively. The addition of rGO filler caused an increase in the electrical conductivity of the electrospinning solution. Hence, the fiber diameter was reduced in the PVDF-rGO composite compared to the pristine PVDF fibers. At a high voltage applied during the electrospinning, the conductive rGO can be easily charged. Hence, the electrostatic repulsion and Coulomb force increased on the Taylor cone, resulting in the subsequent decrease in fiber diameter^[52,66]. Thus, irrespective of the solvents, rGO improved the conductivity and reduced the diameter of the PVDF fiber. The composite PVDF/DMAc-rGO and PVDF/DMF-rGO fibers' annealing shows very similar morphology and fiber diameter, which is evident from the fiber diameter distribution graph, shown in Figures 2a and b.

For the FT-IR spectrum shown in Figures 2c and d, for all the samples, the vibrational bands at 613, 763 and 976 cm^{-1} were the characteristic peaks for the non-polar α phase. Whereas the peaks at 840, 1276 and 1430 cm^{-1} were attributed to the β phase^[21,67]. Compared with the PVDF fibers, the characteristic peak intensities of α phase in electrospun rGO/PVDF composite fibers decreased. The relative fraction of the β phase ($F(\beta)$) for each sample was calculated by analyzing the FTIR results using the following equation (1)^[67];

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

where A_{β} and A_{α} denote absorptions at 840 cm^{-1} and 763 cm^{-1} , respectively. K_{β} and K_{α} represented the absorption coefficients of corresponding wave numbers, which were 6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, respectively^[52,67]. The β phase fraction in the composite fiber incorporating rGO was significantly higher than in the pristine PVDF fiber. Furthermore, with the addition of rGO, the absence or negligible absorbance of α phase at 613, 763, and 976 cm^{-1} was observed. As seen, the intensity of the β phase was increased in the annealed

fibers. However, the intensity of α phase remains the same. In the case of the PVDF/DMAc-rGO composite (Figure 2c), the absorbance intensities of the β phase (840 and 1276 cm^{-1}) were higher than those of the PVDF/DMAc fiber. This result reveals that adding rGO enhances the β phase fraction in the PVDF fibers. The β phase content (%) for PVDF/DMAc and aPVDF/DMAc were found to be 60 % and 63 %, respectively, while incorporating 1wt% of rGO into the PVDF matrix increased the β phase fraction to 69 %. For aPVDF/DMAc-rGO fiber, the increase was 70 % (Table S2, supporting information). About 10% higher amounts of β phase content were obtained for the PVDF/DMAc-rGO composite than for the pristine PVDF fiber.

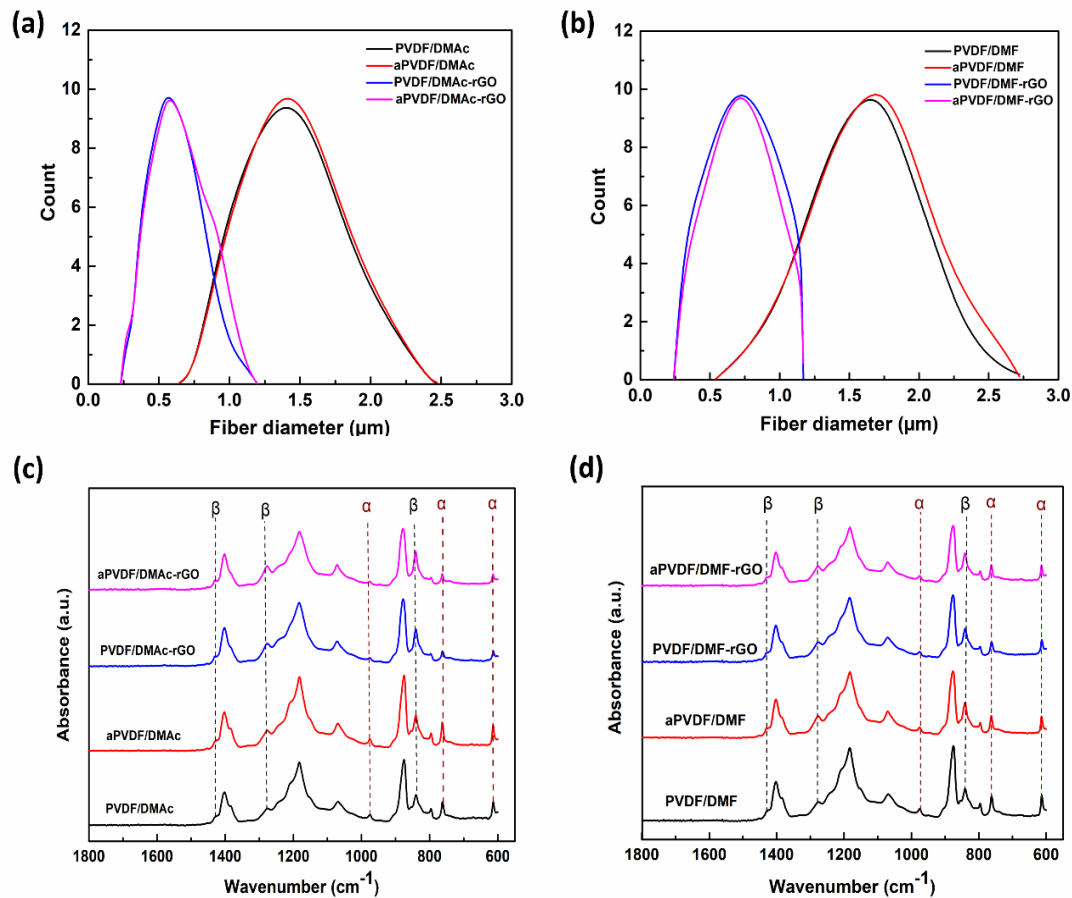
Figure 2(d) represents the FTIR spectra of the PVDF/DMF-rGO composite. Compared with the PVDF fiber prepared in DMAc solvent, the PVDF/DMF fiber exhibits a decrease in β phase content (59 %), whereas an increment in β phase content up to 62 % was observed for the aPVDF/DMF fiber. The absorbance intensity peaks of the β phase were lower for PVDF and PVDF-rGO composite prepared in DMF solvent than for the PVDF/DMAc composite fiber. Additionally, the corresponding α phase peaks at 613, 763, and 976 cm^{-1} were more pronounced in PVDF/DMF and PVDF/DMF-rGO composites compared to the PVDF/DMAc and rGO composites. The addition of rGO and annealing of the composite fibers in DMF solvent led to an increase in the β phase content of 64 %. Figure 3 illustrates the β phase content of all samples from the FTIR analysis. From the FTIR results, we can conclude that PVDF in DMAc solvent is more responsive toward rGO filler and annealing effects. Unlike DMAc solvent, DMF does not respond significantly to filler and the annealing effects. In literature, Yin et al.^[5] studied the effect of solvents (DMF and dimethyl Sulfoxide (DMSO)) and electrospinning parameters on the piezoelectric properties of PVDF polymer. The authors reported that DMSO/Acetone (2/1) solvents showed the highest crystallinity (52.36 %), β phase fraction (88.01 %), and piezoelectric voltage output compared to DMF. Gee et al.^[40] analysed three solvents' effects (DMF, DMSO, NMP) on an electrospun PVDF membrane. Their study revealed that DMF/Acetone exhibited the highest β phase fraction (90.9 ± 1.81 %) among DMSO and NMP. In this study, DMAc/Acetone showed higher β phase content (60 %) than DMF due to the higher electrical conductivity of DMAc. In the case of PVDF-DMAc/rGO, the increased β phase content of 69% can be explained as follows; rGO acted as a nucleating agent and creating a substrate enables the growth of PVDF crystal nucleation and promoting β phase formation

of the PVDF chains by strong interactions at the interface^[68]. In addition, the synergistic effect of electrical conductivity caused by rGO, and DMAc solvent plays a vital role in enhancing the β phase in PVDF-DMAc/rGO.

Further, thermal analysis was carried out using differential scanning calorimetry (DSC) to determine the solvents, annealing, and addition of rGO effects on electrospun PVDF's melting and crystallization behavior. The DSC scans for PVDF/DMAc-rGO and PVDF/DMF-rGO composites are presented in Figures 2e and f. Table 2, in supporting information, shows the melting temperature (T_m), melting enthalpy (ΔH_m), and crystallinity content (χ_c) of all the samples. The crystallinity content (χ_c) of the PVDF fibers was calculated using the following equation^[28].

$$\chi_c = \frac{\Delta H_m}{\Delta H_{100}} \times 100 \quad (2)$$

where ΔH_{100} represents the melting enthalpy of 100% crystalline PVDF ($104.54 \text{ J} \cdot \text{g}^{-1}$)^[28].



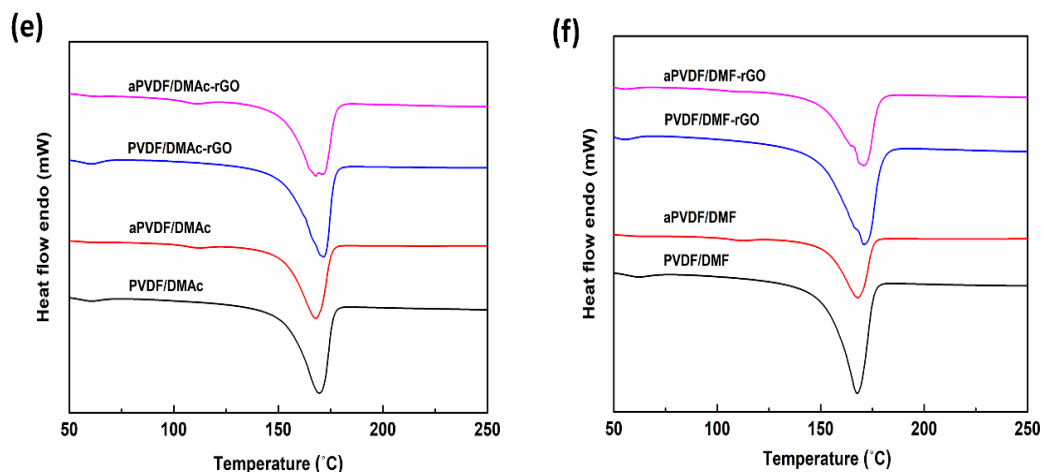


Figure 2. (a) Fiber diameter distribution curve for PVDF/DMAC samples (b) Fiber diameter distribution curve for PVDF/DMF samples (c) FTIR spectra of PVDF/DMAC samples (d) FTIR spectra PVDF/DMF (e) DSC thermograms of PVDF/DMAC and (f) DSC thermograms of PVDF/DMF composites.

From Figure 2 (e), annealing and addition of rGO fillers displayed higher melting enthalpy (ΔH_m) and crystallinity compared to the pristine PVDF/DMAC fibers. PVDF/DMAC exhibited a melting temperature of 169.58 °C, a melting enthalpy of 44.09 J·g⁻¹, and a crystallinity content of 42.17 %. The annealing effect on the electrospun fiber mildly affects the melting enthalpy and, thereby, the crystallinity of the annealed fiber. The slight increment in crystallinity of the annealed fiber can be attributed to the high energy taken from the polymer chains to transform the amorphous form into a crystalline form^[64]. Compared to pristine PVDF fiber, the incorporation of 1wt% of rGO led to a significant increase in T_m (171.57 °C), ΔH_m (50.07 J·g⁻¹), and crystallinity content (47.89 %) of the PVDF composite. This increment in crystallinity indicates that the rGO filler acted as a nucleating agent for the electroactive phases in the PVDF during the electrospinning. This result agrees with the FTIR spectra for PVDF/DMAC-rGO and PVDF/DMF-rGO composites. The higher content of β phase and crystallinity indicates the excellent interaction and affinity between the rGO filler and the PVDF matrix^[69,70].

Kaur et al.^[71] prepared the PVDF thick film by solution casting and investigated the influence of annealing on structural, crystalline, dielectric, and polarization behavior. The study unveiled that annealing PVDF films at 100 °C improve dielectric permittivity and polarization due to an increased crystalline α and β -phase interface. Nevertheless, a few

studies were reported on the annealing effect of PVDF electrospun fibers for energy harvesting applications^[57,64]. Satthiyaraju et al.^[64] examined the annealing of electrospun PVDF at different temperatures. Here, from the graph in Figure 2 (e), it observed a twin peak through the melting response of aPVDF/DMAc-rGO. The annealing of PVDF-rGO causes further amorphization of the polymer fiber and reduces the crystallinity of the composite. Similar trends were observed for the PVDF/DMF-rGO composite (Figure 2f). Compared to PVDF/DMAc, a slight decrease in the melting enthalpy and crystallinity of PVDF/DMF can be observed. Satthiyaraju et al.^[64] reported the increased crystallinity for PVDF nanofibrous film annealed at 100 °C. However, in our study, the annealing at 100 °C showed a slight enhancement in crystallinity regardless of the solvent used. Additionally, no comprehensive study has been reported on the annealing effect of PVDF-rGO composite electrospun fibers. Similar to FTIR results, Yin et al.^[5] reported the higher crystallinity content from DSC for DMSO/Acetone than DMF/Acetone. It confirms that the solution with higher conductivity shows improved β -phase content and crystallinity.

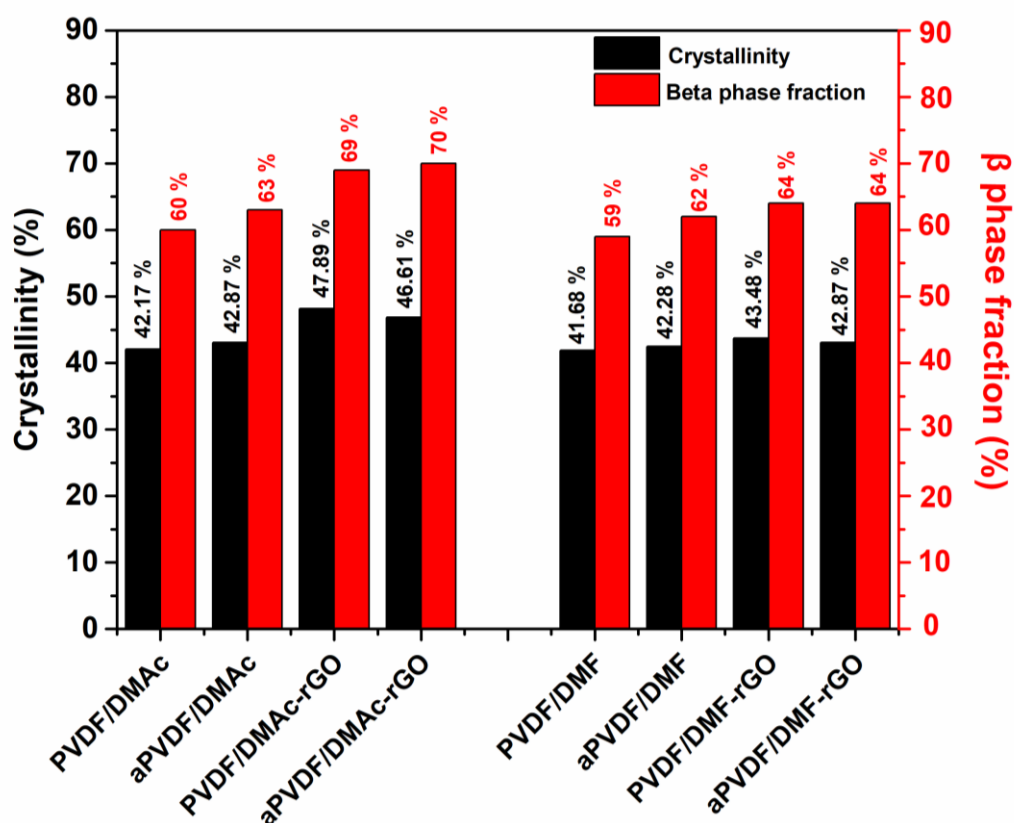


Figure 3. Relationship between crystallinity and β phase fraction of PVDF fiber mats.

Figure 3 presents the relationship between crystallinity and β phase fraction of all the PVDF fibers and composites. All types of PVDF samples with DMAc show higher crystallinity and β phase. Adding rGO to the PVDF/DMF raises the crystallinity from 41.68% to 43.48%. However, compared with the PVDF/DMAc-rGO, the PVDF/DMF-rGO showed a lower crystallinity content. Corresponding to the aPVDF/DMAc-rGO composite, aPVDF/DMF-rGO also displayed a decrease in crystallinity compared to PVDF/DMF-rGO. This result further confirms the amorphization of the composite after annealing. Importantly, FTIR and DSC confirm that adding 1 wt% of rGO into PVDF/DMAc leads to the highest content of β phase and crystallinity.

Interestingly, the annealing effects on the fibers were not prominent in DMAc or DMF solvents. Also, for PVDF/rGO composites, the annealing effect reduces the crystallinity irrespective of the solvents. Therefore, we selected PVDF/DMAc, PVDF/DMAc-rGO, PVDF/DMF, and PVDF/DMF-rGO samples to further verify the piezoelectric response of the electrospun fibers by using the high voltage switching spectroscopy piezoelectric force microscopy (HVSS-PFM). The topographic images of the fibers from atomic force microscopy (AFM) are shown in Figure S2 in the supporting information. The AFM images agree with the SEM results that rGO filler reduces the fiber diameter of PVDF fibers. HVSS-PFM data presented in Figure 4 for PVDF/DMAc, PVDF/DMAc-rGO, PVDF/DMF, and PVDF/DMF-rGO were measured by applying the voltage from -30 to +30 V by keeping the tip at a fixed point on the surface of the PVDF single fiber. In Figure 4, the PFM phase and amplitude loops are presented, and from them, the hysteresis behavior under the effect of an electric field was determined. The PFM phase vs voltage graph for PVDF/DMAc and PVDF/DMAc-rGO, in Figure 4a, exhibits a square-shaped hysteresis loop with a 180° phase shift between the positive and negative voltages. Figure 4b shows the amplitude vs voltage butterfly curve for PVDF/DMAc and PVDF/DMAc-rGO. The forward and reverse coercive voltages were obtained at +14 V and -14 V, respectively, for PVDF/DMAc. At a DC bias of 60 V, the maximum amplitude reached 106 ± 3 pm. In the case of PVDF/DMAc-rGO, the highest amplitude value was 104 ± 2 pm. Correspondingly, the forward and reverse coercive electric fields were noted at +17 V and -4 V, respectively. PVDF/DMAc-rGO fiber has a narrower butterfly loop than PVDF/DMAc fiber, indicating that a smaller electric field was required to generate a piezoelectric response to switch the polarization.

For PVDF/DMF and PVDF/DMF-rGO fibers, the butterfly loops, and hysteresis curves, presented in Figure 4 c and d were qualitatively similar to PVDF/DMAc fibers with a phase change of 180° . However, PVDF/DMF showed a lower maximum amplitude value of $69 \text{ pm} \pm 4$ (Figure 4d) with a forward coercive field of 1 V and reverse coercive field of -26 V. Adding rGO increased the amplitude value for PVDF/DMF and obtained the peak amplitude value of $76 \text{ pm} \pm 3$. PVDF/DMF-rGO also showed a narrow hysteresis curve with a forward and reverse coercive voltage of 11 V and -7 V, respectively. This result confirms that adding rGO reduces the electric field required to switch the polarization of PVDF and provides an enhanced piezoelectric response. Additionally, we must note that the amplitude value may change according to the different cantilevers and microscopes used to measure the fiber response.

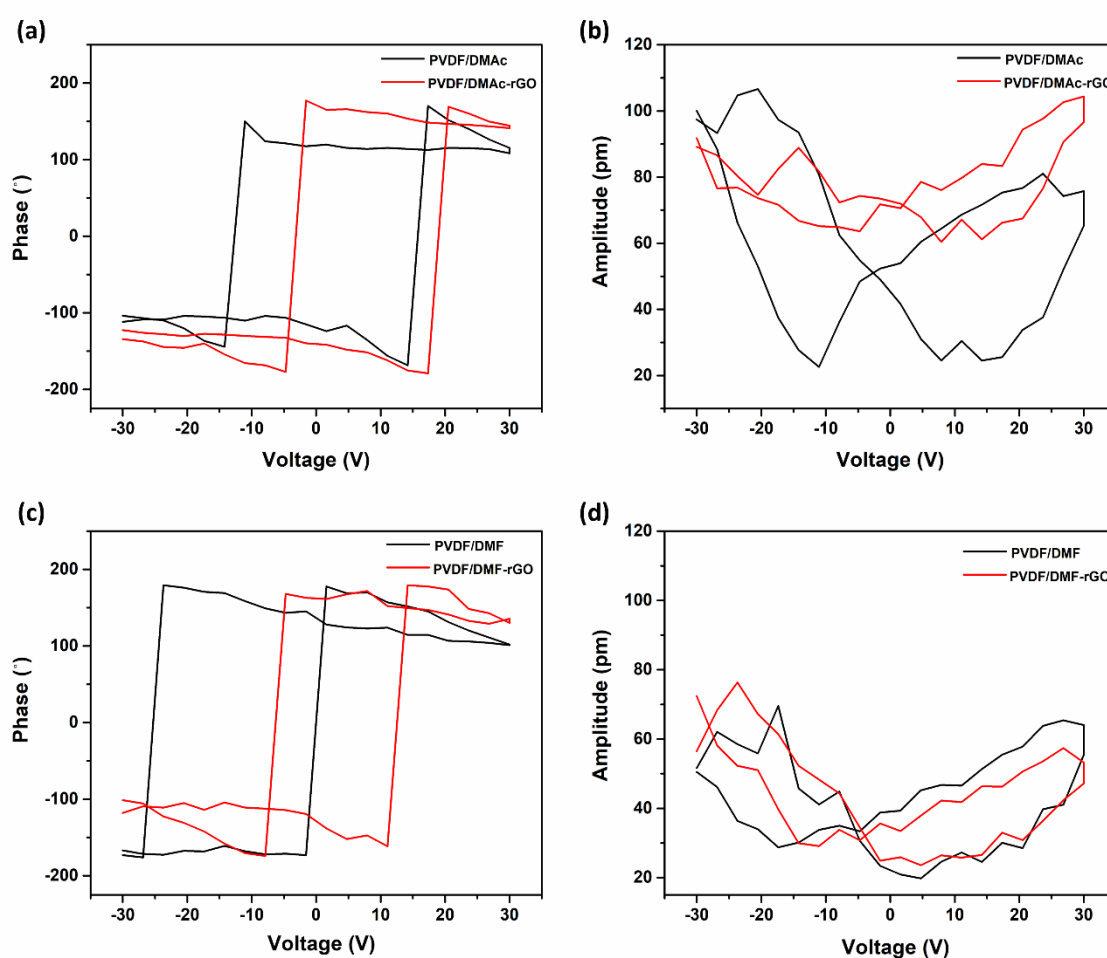


Figure 4. HVSS-PFM spectroscopy curves showing the piezo-response for PVDF fiber, phase vs voltage (left) and amplitude vs voltage (right). (a) PVDF/ DMAc and PVDF/ DMAc-rGO phase (b) PVDF/ DMAc and PVDF/ DMAc-rGO amplitude (c) PVDF/ DMF and PVDF/ DMF-rGO phase (d) PVDF/ DMF and PVDF/ DMF-rGO amplitude.

Moreover, the piezoelectric coefficient (d_{33}) measurements were carried out to understand the relationship between the crystallization and piezoelectricity for bulk fiber mats. Table S3 in the supporting information lists the d_{33} values of all PVDF mats and the amplitude values from HVSS-PFM. The d_{33} values of PVDF/DMAc and PVDF/DMAc-rGO, PVDF/DMF and PVDF/DMF-rGO are $7.3 \pm 0.2 \text{ pC/N}$, and $11.9 \pm 0.2 \text{ pC/N}$, $5.6 \pm 0.2 \text{ pC/N}$ and $7.2 \pm 0.2 \text{ pC/N}$ respectively, see Figure 5. This result agrees well with the FTIR and DSC results, where PVDF/DMAc-rGO fiber has the highest β phase content and crystallinity. Therefore, it displayed a higher d_{33} value. From the literature studies, we can find that in the case of electrospun fibers, the type of electrode coating affects the obtained value of the d_{33} coefficient^[72,73]. Most literature studies lack information regarding the electrode material used to measure the d_{33} piezoelectric coefficient. However, considering the porosity of the electrospun fiber mat (approximately 90 %)^[74,75] for the d_{33} measurements, the contact electrode is mostly measuring the air. Therefore, the d_{33} cannot be expected to be as high as for typically spin-coated or casted PVDF films^[24,76].

From our study, using DMAc as a solvent and adding rGO as filler is the most promising strategy for electrospun PVDF mats to obtain high efficiency in energy harvesting or sensing applications. Notably, the highest conductivity of DMAc ($0.300 \pm 0.013 \text{ }\mu\text{Scm}^{-1}$) over DMF ($0.241 \pm 0.013 \text{ }\mu\text{Scm}^{-1}$) and just 1% addition of rGO is able to increase the β phase fraction over standard PVDF by 9 %. Figure 5 shows the relation between the piezoelectric coefficient of the PVDF mats, β phase fraction of the mats, and the amplitude of the single PVDF fibers. The amplitude values between PVDF/DMAc and PVDF/DMAc-rGO were almost similar. Therefore, the difference in the performance between the individual fibers and mats for the PVDF/DMAc-rGO individual fibers measured using HVSS-PFM can be related to the enhancement of piezoresponse performance when more fibers are in contact with the mat. In addition, the random distribution of rGO for the whole mat has an intensified effect than in the individual fibers.

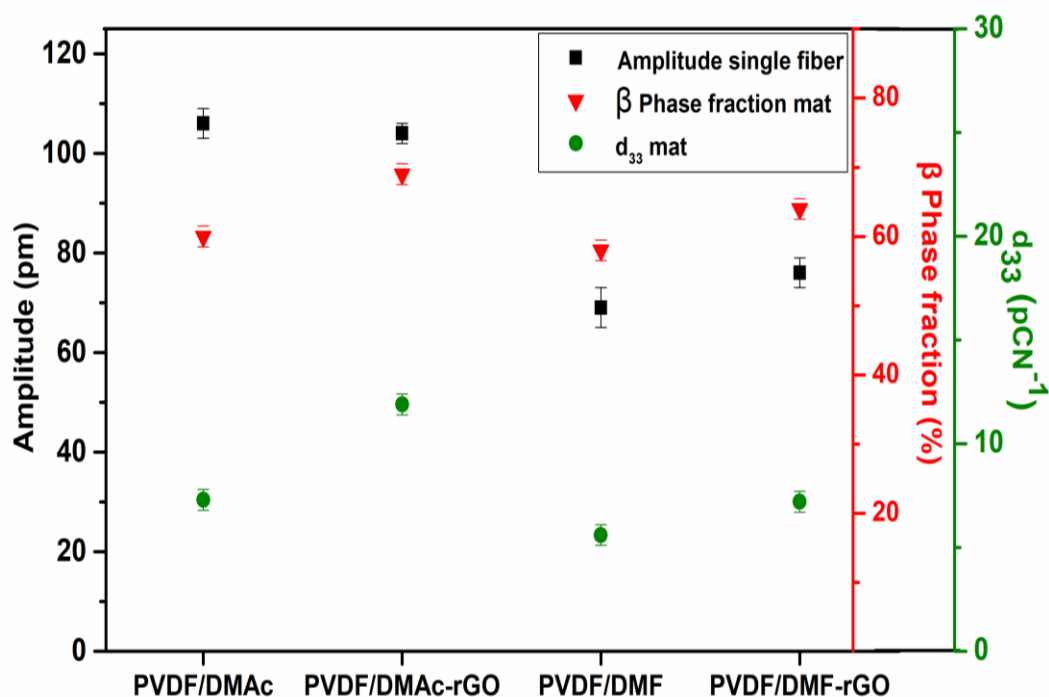


Figure 5. Relation between the piezoelectric coefficient of the mat, amplitude response of single fiber from HVSS-PFM, and β phase fraction of the mat.

From the above characterization studies and discussions, it is evident that the higher electroactive β phase is induced in electrospun fiber in DMAc solvent and the presence of rGO particles. Thus, PVDF/DMAc-rGO mat is suitable for fabricating a piezoelectric energy harvester to convert mechanical energy that can be used. We have selected PVDF/DMAc as a reference material to compare the energy harvesting performance of the PVDF/DMAc-rGO device. A detailed description of the device fabrication was given in the experimental section. The piezoelectric responses of the fabricated device were recorded by applying repeated human finger tapping and releasing movements, see the Movie S1 in the Supporting Information. Figure 6 a-d presented the open circuit voltage and short circuit current signals obtained from PVDF/DMAc and 1 wt% PVDF/DMAc-rGO composite under finger tapping and releasing. The device can convert the finger tapping motion (mechanical movements) into electricity by repeated pressing and releasing movements^[24]. By finger tapping we change in polarization of the PVDF, a piezoelectric potential is developed between the two electrodes. Simply, the potential difference is causing transitory passing of the free electrons from one electrode to another, leading to a positive voltage peak. The instant release of stress caused by the finger press, a negative

output voltage appears owing to the decrease in the piezo potential and discharging of the accrued electrons^[24]. From Figures 6 a and b, PVDF/DMAc-rGO showed a higher output voltage (6 ± 1.4 V) than of pure PVDF/DMAc (3.4 ± 1 V). Similarly, the current signals exhibited more than double output value of 320 ± 81 nA from the PVDF/DMAc-rGO (Figure 6d).

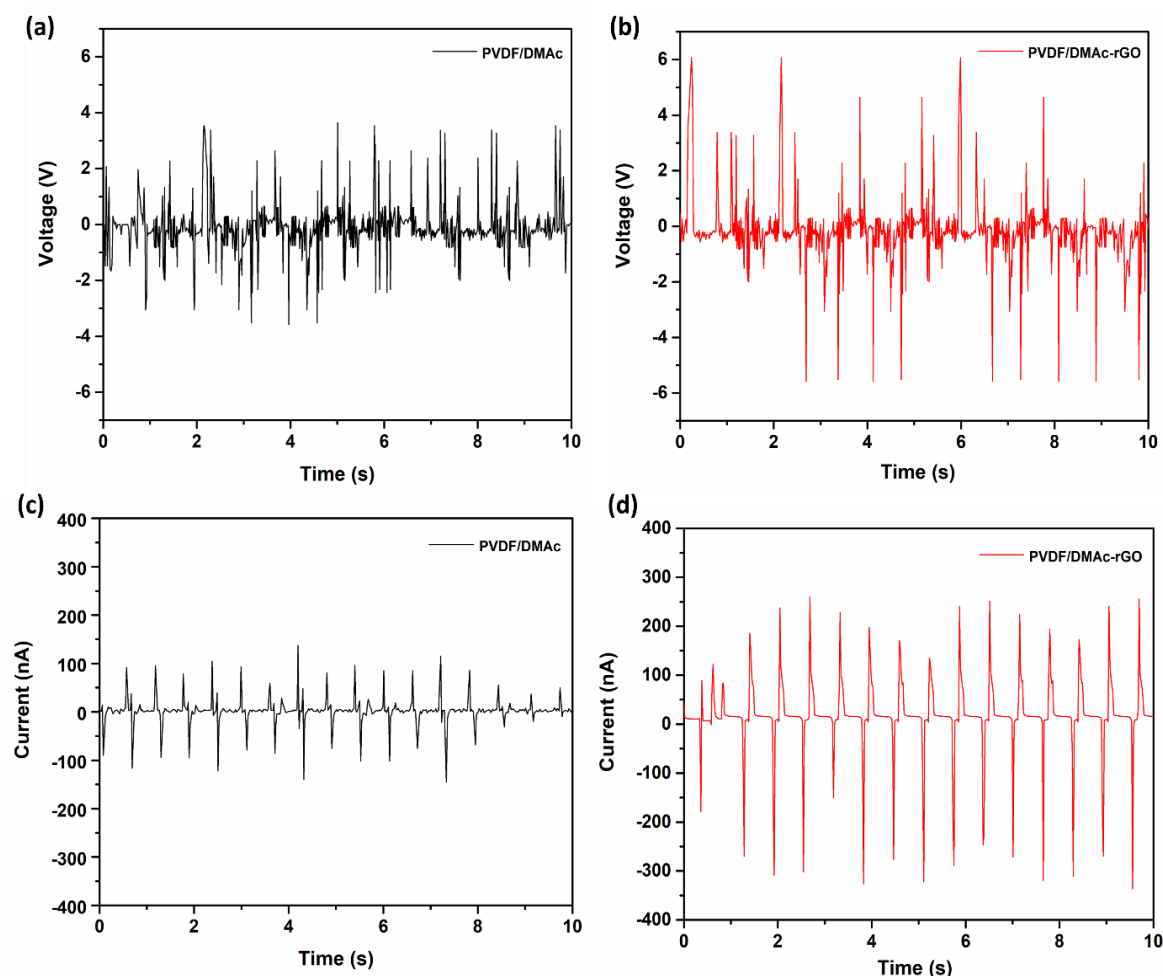


Figure 6. (a) Piezoelectric output voltage measurement of PVDF/DMAc (b) Output voltage from PVDF/DMAc-rGO (c) current output of PVDF/DMAc (d) current output of PVDF/DMAc-rGO.

The PVDF/DMAc displayed an output current of 133 ± 45 nA (Figure 6 c). The higher output voltage and current signals from PVDF/DMAc-rGO can be explained by the highest amplitude and piezoelectric coefficient values from HVSS-PFM and d_{33} studies. Furthermore, rGO promoted and induced the nucleation of electroactive β -phase in the PVDF matrix as described in the DSC section. In addition, rGO creates a conduction network that efficiently diminishes the internal resistance of the piezo device^[77,78].

Subsequently, it enhances the transfer of induced charge produced by PVDF and thus exhibits the high piezoelectric performance of the device^[52]. Also, rGO causes an increase in the conductivity of the PVDF solution during electrospinning, and it helps to provide more nucleation sites and increase the PVDF's electrical properties^[52,66]. Here, for PVDF/DMAc-rGO, the combined effect of DMAc solvent with higher conductivity and rGO filler's electrical conductivity improves the piezoelectric performance. Further, the power density of the piezo device was calculated, see Figure 7 (a) illustrates the power densities of PVDF and rGO/PVDF composite. PVDF/DMAc gives a power density of $0.452 \pm 0.21 \mu\text{W}\cdot\text{cm}^{-2}$, and PVDF/DMAc-rGO showed an increased power density of $1.92 \pm 0.71 \mu\text{W}\cdot\text{cm}^{-2}$, which is more than 4 times higher.

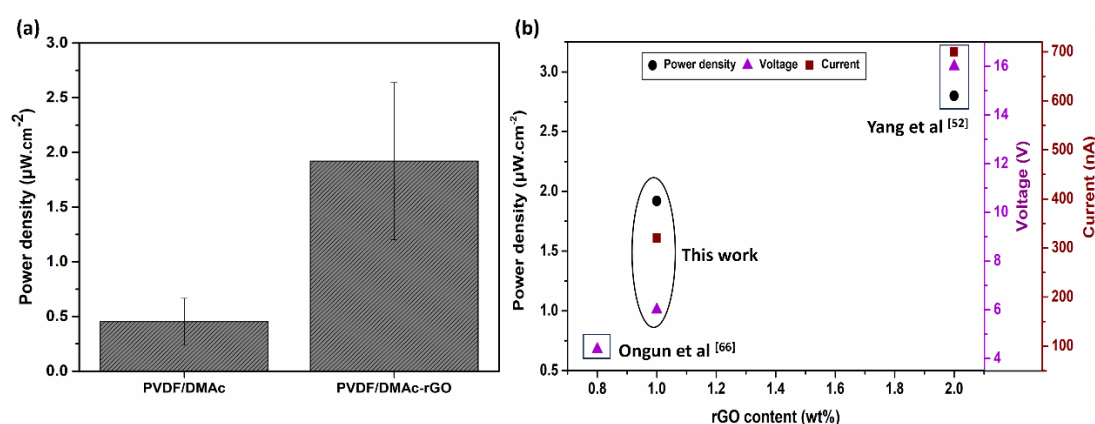


Figure 7. (a) Power density of PVDF/DMAc and PVDF/DMAc-rGO. (b) PVDF/rGO composites energy harvesting performance comparison from literature and this work.

Previously, a few studies have been reported on PVDF/rGO electrospun composite. A comparison graph with the rGO content and the energy harvesting outputs (power density, voltage, and current) values from the literature and the results obtained in this work are illustrated in Figure 7(b). Ongun et al.^[66], demonstrated the finger tapping and releasing test on PVDF and rGO/PVDF composites with 0.4 and 0.8 wt% rGO loading. The solvents used to prepare the electrospun PVDF and composites are DMF and acetone (1:1 v/v). The results indicated that 0.8 wt % rGO/PVDF has the highest β phase content and generated an output voltage of 4.38 V which is approximately 9 times higher than pure PVDF (0.50 V). However, there is no information regarding the generated current and power output values. Yang et al.^[52], fabricated the piezoelectric nanogenerator (PENG) based on electrospun PVDF and PVDF/rGO nanocomposite, using DMF solvent and rGO additions 1, 1.5, and 2 wt%. The authors reported that, under finger pressing, the 2wt% rGO-PVDF

had reached a short circuit current of 700nA, voltage of 16 V, and a power density of 2.8 $\mu\text{W}.\text{cm}^{-2}$ for a film area of 6.25 cm^2 . The power density for 2wt% rGO-PVDF is 150 times higher than pristine PVDF (18.75 $\text{nW}.\text{cm}^{-2}$). In this study, an active PVDF fiber area of $1\times 1\text{ cm}^2$ under finger tapping reaches a power density of 0.452 $\mu\text{W}.\text{cm}^{-2}$, voltage, and current output of 3.4 V, and a current of 133 nA. Therefore, the results again proved that the PVDF fibers prepared in DMAc solvent have better piezoelectric performance than DMF. In addition, from our studies, 1 wt % rGO generated a power density of $1.92 \pm 0.71\text{ }\mu\text{W}.\text{cm}^{-2}$ for an area of only $1\times 1\text{ cm}^2$. Hence, these results supported that the PVDF/DMAc-rGO had enhanced piezoelectric properties that can be applied in energy harvesting and sensor applications.

3. Conclusion

In this study, we verify different strategies, such as the effect of most used solvents (DMAc, DMF), annealing, and addition of rGO filler to electrospun PVDF membrane to control the piezoelectric response. By comparing all three effects, the addition of rGO showed the highest crystallinity, β phase fraction, and piezoelectric coefficient compared to annealing. On the contrary, for the composite fibers (PVDF/DMAc-rGO, PVDF/DMF-rGO), annealing reduces the crystallinity and β phase fraction due to the amorphization of the polymer fiber. In literature, DMF is the most used solvent for PVDF electrospinning. However, from our findings, DMAc exhibited a higher piezoelectric response compared to DMF due to the higher conductivity of DMAc. Also, adding rGO to PVDF/DMAc has a noticeable impact on the piezoelectric response. The FTIR and DSC results revealed that PVDF/DMAc-rGO presented the highest crystallinity, β phase fraction, and piezoelectric coefficient. Here, rGO acted as a nucleating agent and induced the PVDF chain's β phase formation. For the first time, we are reporting the piezoelectric properties of PVDF/rGO single electrospun fiber in DMAc and DMF solvents by using the HVSS-PFM technique. The HVSS-PFM results further confirm the FTIR and DSC results and have the highest amplitude for PVDF/DMAc-rGO fiber.

Nonetheless, in alignment with FTIR and DSC results, PVDF/DMF-rGO has not significantly improved the piezoelectric coefficient compared to PVDF/DMF fiber from the HVSS-PFM study. Therefore, to present the best combination among the methods

mentioned above and make it useful at the application level, we have measured the d_{33} value of the PVDF membrane. From d_{33} measurements, we again confirm that PVDF/DMAc-rGO reported the highest value of $11.9 \pm 0.2 \text{ pC}\cdot\text{N}^{-1}$ and PVDF/DMAc of $7.3 \pm 0.2 \text{ pC}\cdot\text{N}^{-1}$. Therefore, by comparing different strategies to control the piezoelectric properties of PVDF electrospun fiber, we found that the best method is to use DMAc as the solvent and conductive filler (rGO) for energy harvesting applications. Therefore, by comparing different strategies to control the piezoelectric properties of PVDF electrospun fiber, we found that the best method is to use DMAc as the solvent and conductive filler (rGO) for energy harvesting applications. The finger-tapping test was conducted to show the straightforward practical application of the PVDF/DMA-rGO mat. The results revealed that 1 wt% rGO content achieved a power density of $1.92 \pm 0.71 \mu\text{W}\cdot\text{cm}^{-2}$, which is more than 4 times higher than pure PVDF. The rGO with high conductivity enhanced transferring of induced charge generated by PVDF, thereby improving the piezoelectric energy harvesting and conversion ability of PVDF.

4. Experimental section

Materials and electrospinning

PVDF pellets ($M_w = 275,000 \text{ g mol}^{-1}$) were purchased from Sigma- Aldrich, UK. Reduced graphene oxide (rGO, thickness 0.5-2 nm) was supplied by Nanografi, Turkey. Dimethylacetamide (DMAc), Dimethylformamide (DMF) and Acetone were purchased from analytical standard, Avantor, Poland.

PVDF pellets were dissolved in DMAc/Acetone solvent in a 1:1 (wt/wt) ratio by constant magnetic stirring. The temperature was set at 55°C on a hot plate (IKA RCT basic, Germany) for 4 h at a constant speed of 650 rpm to prepare a homogenous 24 wt% PVDF/DMAc solution. Similarly, the PVDF/DMF solution of 24 wt% was prepared by dissolving PVDF pellets in DMF and acetone (1:1 wt/wt). The solution was stirred on a hotplate at 55°C for 4 h at a speed of 650 rpm. Then, the 1 wt% of rGO was added to the PVDF/DMAc and PVDF/DMF solutions in the following ways to obtain the PVDF/DMAc-rGO and PVDF/DMF-rGO solutions, respectively. First, by ultrasonication (Emag, Emmi-E20, Germany) for 4 h, rGO was dispersed in DMAc and an acetone mixture (1:1). Subsequently, it was added to the prepared PVDF/DMAc (24 wt%) solution and the reaction mixture was stirred for 2 h at 55

513 °C. Finally, the PVDF/DMAc-rGO solution was subjected to ultrasonication for 2 h prior to
 514 electrospinning. Correspondingly, the PVDF/DMF-rGO solution was prepared in the same
 515 way. Firstly, the rGO was dispersed in the DMF/Acetone mixture (1:1) by ultrasonication for
 516 4 h, added to the PVDF/DMF (24 wt%) solution, and stirred for 2 h at 55 °C. Lastly,
 517 ultrasonication was carried out for 2 h to obtain a homogenized dispersion of rGO in the
 518 PVDF/DMF solution before electrospinning.

519
 520 Electrospinning of PVDF and the PVDF-rGO composites in DMF and DMAc solutions was
 521 carried out with SKE Technologies (Italy) with the climate control system. Electrospinning
 522 was initiated by loading the PVDF/DMAc solution in a syringe (5 mL) connected with a
 523 stainless needle with an outer diameter of 0.8 mm and an inner diameter of 0.5mm. A positive
 524 voltage polarity (+18 kV) was applied to the needle to electrospun PVDF/DMAc and
 525 PVDF/DMAc-rGO solutions. The flow rate was set at 1 ml.h⁻¹ with a distance of 18 cm
 526 between the needle tip to the grounded collector plate for the PVDF/DMAc and PVDF/DMAc-
 527 rGO solutions. The electrospun PVDF/DMF fibers were produced by applying a positive
 528 voltage of 20 kV with a flow rate of 1 ml⁻¹.h at a distance of 18 cm from the collector plate.
 529 PVDF/DMF-rGO solution electrospinning was carried out by applying +18 kV with a flow
 530 rate of 1 ml⁻¹. h and and kept at the distance of the needle tip to the collector plate at 20 For all
 531 samples, ambient temperature and relative humidity (RH) during the electrospinning were kept
 532 constant at 25 °C and 30%, respectively. The electrospinning parameters for all the samples
 533 are summarized in supporting information (Table S1). In addition, the physical properties of
 534 the solvents are presented in supporting information (Table S4).

535
 536 The produced fibers were collected on Al foil for SEM, FTIR, and DSC analysis. For PFM
 537 measurements, the fibers were electrospun directly on Indium tin oxide (ITO) glass.

538

539 **Postprocessing treatment**

540

541 After fabricating electrospun PVDF fibers and PVDF/rGO composite in DMAc and DMF
 542 solvents, the samples were kept at room temperature (24 °C). It helps to remove any residual
 543 solvents that may be present in the electrospun fibers. The as-obtained PVDF/DMAc,
 544 PVDF/DMAc-rGO, PVDF/DMF, and PVDF/DMF-rGO electrospun fibers were annealed at
 545 100 °C in an airflow oven for 3h. The morphology, β phase content, crystallinity, and

546 piezoelectric response of the annealed samples were compared with those of the electrospun
547 fibers.

548

549 **Preparation of piezo device**

550

551 The piezo device consisted of a 1×1 cm active layer of PVDF mat sandwiched between an Al
552 foil as electrodes on both sides of the mat. A copper tape was used to take the connection from
553 both electrodes to measure the generated voltage and current. The voltage and current
554 measurements were conducted with three samples for each material and the average values
555 were taken.

556

557 **Characterization of electrospun fibers**

558 **Scanning electron microscopy (SEM)**

559

560 The morphology of the PVDF fibers was evaluated using SEM (Merlin Gemini II, Zeiss,
561 Germany) at an accelerating voltage of 3 kV and a working distance of 6 mm. Before imaging,
562 all samples were Au coated with a thickness of 8 nm using a rotary pump sputter coater
563 (Q150RS, Quorum Technologies, UK). The fiber diameters (D_f) were measured from SEM
564 micrographs utilizing the ImageJ (v. 1.53c, USA) software and correlated into a histogram
565 provided with standard deviation.

566

567 **Conductometer**

568

569 The conductivity of all solvents was measured with a Mettler Toledo Conductometer (Seven
570 Compact S210, Zurich, Switzerland). Five measurements were taken for each solvent, and the
571 average value was taken.

572

573 **Fourier transform infrared spectroscopy (FTIR)**

574

575 FTIR was performed to analyze the crystallinity and distinguish the different phases in PVDF
576 fibers. Nicolet iS5 FT-IR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA),
577 with a Ge crystal, was used to conduct the spectroscopy by the ATR technique. During
578 measurements, 64 spectra were repeated with a resolution of 1 cm^{-1} over the wavenumber
579 range from 600 to 4000 cm^{-1} . Three measurements were carried out for each sample.

580

581 **Differential scanning calorimetry (DSC)**

582

583 Thermal characterization was performed using a differential scanning calorimeter (Mettler
584 Toledo, Columbus, OH, USA) at a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ in the 50 to $270\text{ }^{\circ}\text{C}$ temperature
585 range. The samples were placed in an Al pan, and the measurements were carried out in a
586 dynamic Ar atmosphere. For each sample, three tests were performed.

587

588 **Piezoelectric force microscopy (PFM)**

589

590 The piezoelectric response of single electrospun PVDF fibers and their composites was
591 analyzed using CoreAFM (Nanosurf, Switzerland). The samples for PFM measurements were
592 prepared by electrospinning the PVDF fibers directly on the ITO substrate (Ossila, Germany).

593

594 For the measurements, a conductive Pt/Si coated Si cantilever (nanosensors, Switzerland) was
595 used with a spring constant of 2.15 Nm^{-1} and a resonance frequency of 6 kHz. The topography
596 images were obtained in static PFM mode by applying an AC voltage of 10 V between the
597 cantilever tip and the bottom electrode. The amplitude and phase of the piezoresponse of the
598 fiber were measured by applying a sequence of pulses of DC bias voltage. The spectroscopic
599 technique helps to identify the required voltage for domain switching. This study used a high-
600 voltage (HV) amplifier connected to the user output to achieve the coercive electric field. DC
601 pulses between -30 V to +30 V were applied through the HV amplifier to induce the
602 piezoelectric response. We use tip bias for electrical pulses with a voltage range of 60 V within
603 20 steps and a pulse time of 0.05 s. The PFM measurements were performed in "on and off
604 states," indicating the DC bias voltage status. Here, AC voltage is continuously applied to
605 measure the piezoelectric signal, and the DC voltage is applied to change the polarization
606 during domain switching. This method helps to reduce the electrostatic effect^[79]. SS-PFM
607 measurements were performed with three different individual fibers.

608

609 **Piezoelectric d_{33} meter**

610

611 The piezoelectric coefficients of the electrospun PVDF membrane were examined with a d_{33}
612 meter (YE2730A d_{33} meter, Sinocera, China). This instrument is designed specifically for

613 directly measuring the d_{33} values of piezoelectric materials. 20 nm Au layer was coated as an
 614 electrode on both sides of the PVDF fiber for the test. Five measurements were performed for
 615 each sample, and the average d_{33} value was taken.

616

617 The voltage and current value from the piezo device were measured by a Keithley DMM6500
 618 6 1/2 digital multimeter (China).

619

620 **Acknowledgment**

621

622 This study was conducted as part of the BioCom4SavEn project funded by the European
 623 Research Council under the European Union's Horizon 2020 Framework Programme for
 624 Research and Innovation (ERC grant agreement no. 948840).

625

626 **Conflict of interest**

627

628 The authors declare that they have no known competing financial interests or personal
 629 relationships that could have appeared to influence the work reported in this paper. The
 630 raw/processed data required to reproduce this finding are available on request.

631

632 **Reference**

633

- 634 [1] K. Castkova, J. Kastyl, D. Sobola, J. Petrus, E. Stastna, D. Riha, P. Tofel, *Nanomaterials*
 635 **2020**, *10*, 1221.
- 636 [2] M. Smith, S. Kar-Narayan, *Int. Mater. Rev.* **2022**, *67*, 65.
- 637 [3] A. Ivanoska-Dacikj, U. Stachewicz, *Rev. Adv. Mater. Sci.* **2020**, *59*, 487.
- 638 [4] F. R. Fan, W. Tang, Z. L. Wang, *Adv. Mater.* **2016**, *28*, 4283.
- 639 [5] J.-Y. Yin, C. Boaretti, A. Lorenzetti, A. Martucci, M. Roso, M. Modesti, *Nanomaterials*
 640 **2022**, *12*, 962.
- 641 [6] D.-J. Shin, S.-J. Jeong, C.-E. Seo, K.-H. Cho, J.-H. Koh, *Ceram. Int.* **2015**, *41*, S686.
- 642 [7] J. Roscow, R. Lewis, J. Taylor, C. Bowen, *Acta Mater.* **2017**, *128*, 207.
- 643 [8] A. Yang, Y. Qiu, D. Yang, K. Lin, S. Guo, *RSC Adv.* **2021**, *11*, 3363.
- 644 [9] C.-H. Wang, W.-S. Liao, Z.-H. Lin, N.-J. Ku, Y.-C. Li, Y.-C. Chen, Z.-L. Wang, C.-P.
 645 Liu, *Adv. Energy Mater.* **2014**, *4*, 1400392.

- 646 [10] M. Wu, T. Zheng, H. Zheng, J. Li, W. Wang, M. Zhu, F. Li, G. Yue, Y. Gu, J. Wu, *J.*
 647 *Mater. Chem. A* **2018**, 6, 16439.
- 648 [11] S. Sukumaran, S. Chatbouri, D. Rouxel, E. Tisserand, F. Thiebaud, T. Ben Zineb, *J. Intell.*
 649 *Mater. Syst. Struct.* **2020**, 1045389X20966058.
- 650 [12] M. Zheng, Y. Hou, X. Yan, L. Zhang, M. Zhu, *J. Mater. Chem. C* **2017**, 5, 7862.
- 651 [13] S. Mishra, L. Unnikrishnan, S. K. Nayak, S. Mohanty, *Macromol. Mater. Eng.* **2019**, 304,
 652 1800463.
- 653 [14] M. T. Chorsi, E. J. Curry, H. T. Chorsi, R. Das, J. Baroody, P. K. Purohit, H. Ilies, T. D.
 654 Nguyen, *Adv. Mater.* **2019**, 31, 1802084.
- 655 [15] M.-H. Zhao, Z.-L. Wang, S. X. Mao, *Nano Lett.* **2004**, 4, 587.
- 656 [16] M. Kim, S. Lee, Y. Kim, *APL Mater.* **2020**, 8, 071109.
- 657 [17] P. Martins, A. C. Lopes, S. Lanceros-Mendez, *Prog. Polym. Sci.* **2014**, 39, 683.
- 658 [18] Q. Zheng, B. Shi, Z. Li, Z. L. Wang, *Adv. Sci.* **2017**, 4, 1700029.
- 659 [19] J. Yan, M. Liu, Y.G. Jeong, W. Kang, L. Li, Y. Zhao, N. Deng, B. Cheng, G. Yang,
 660 G. Nano Energy **2019**, 56, 662-692.
- 661 [20] L. Ruan, X. Yao, Y. Chang, L. Zhou, G. Qin, X. Zhang, *Polymers* **2018**, 10, 228.
- 662 [21] X. Cai, T. Lei, D. Sun, L. Lin, *RSC Adv.* **2017**, 7, 15382.
- 663 [22] Z. Yin, B. Tian, Q. Zhu, C. Duan, *Polymers* **2019**, 11, 2033.
- 664 [23] K. Ke, P. Pötschke, D. Jehnichen, D. Fischer, B. Voit, *Polymer* **2014**, 55, 611.
- 665 [24] S. Sukumaran, S. Chatbouri, L. Badie, F. Thiebaud, T. Ben Zineb, D. Rouxel, *J. Intell.*
 666 *Mater. Syst. Struct.* **2022**, 1045389X221111550.
- 667 [25] Y. Lin, Y. Zhang, F. Zhang, M. Zhang, D. Li, G. Deng, L. Guan, M. Dong, *Nanoscale*
 668 *Res. Lett.* **2021**, 16, 79.
- 669 [26] P. K. Szewczyk, A. Gradys, S. K. Kim, L. Persano, M. Marzec, A. Kryshnal, T. Busolo,
 670 A. Toncelli, D. Pisignano, A. Bernasik, S. Kar-Narayan, P. Sajkiewicz, U. Stachewicz,
 671 *ACS Appl. Mater. Interfaces* **2020**, 12, 13575.
- 672 [27] D. Ponnammam, O. Aljarod, H. Parangusan, M. A. Ali Al-Maadeed, *Mater. Chem. Phys.*
 673 **2020**, 239, 122257.
- 674 [28] M. S. Ramasamy, *Ceram. Int.* **2021**, 12.
- 675 [29] D. P. Ura, U. Stachewicz, *Macromol. Mater. Eng.* **2022**, 307, 2100843.
- 676 [30] P. K. Szewczyk, D. P. Ura, S. Metwally, J. Knapczyk-Korczak, M. Gajek, M. M. Marzec,
 677 A. Bernasik, U. Stachewicz, *Polymers* **2019**, 11, 34.

- 678 [31] G.-Z. Yang, H.-P. Li, J.-H. Yang, J. Wan, D.-G. Yu, *Nanoscale Res. Lett.* **2017**, 12, DOI
679 10.1186/s11671-016-1824-8.
- 680 [32] P. K. Szewczyk, U. Stachewicz, *Adv. Colloid Interface Sci.* **2020**, 286, 102315.
- 681 [33] J. Han, L. Xiong, X. Jiang, X. Yuan, Y. Zhao, D. Yang, *Prog. Polym. Sci.* **2019**, 91, 1.
- 682 [34] P. K. Szewczyk, D. P. Ura, U. Stachewicz, *Fibers* **2020**, 8, 65.
- 683 [35] D. P. Ura, J. Knapczyk-Korczak, P. K. Szewczyk, E. A. Sroczyk, T. Busolo, M. M. Marzec,
684 A. Bernasik, S. Kar-Narayan, U. Stachewicz, *ACS Nano* **2021**, 15, 8848.
- 685 [36] G. Kalimuldina, N. Turdakyn, I. Abay, A. Medeubayev, A. Nurpeissova, D. Adair, Z.
686 Bakenov, *Sensors* **2020**, 20, 5214.
- 687 [37] H. Shao, J. Fang, H. Wang, T. Lin, *RSC advances* **2015**, 19, 14345-14350.
- 688 [38] Z. He, F. Rault, M. Lewandowski, E. Mohsenzadeh, F. Salaün, *Polymers* **2021**, 13, 174.
- 689 [39] J. Zheng, A. He, J. Li, C. C. Han, *Macromol. Rapid Commun.* **2007**, 28, 2159.
- 690 [40] S. Gee, B. Johnson, A. L. Smith, *J. Membr. Sci.* **2018**, 563, 804.
- 691 [41] M. Wang, Z. Jiao, Y. Chen, X. Hou, L. Fu, Y. Wu, S. Li, N. Jiang, J. Yu, *Compos. Part*
692 *Appl. Sci. Manuf.* **2018**, 109, 321.
- 693 [42] K. Čech Barabaszová, S. Holešová, L. Plesník, Z. Kolská, K. Jozsko, B. Gzik-Zroska,
694 *Polymers* **2022**, 14, 3831.
- 695 [43] F.-C. Chiu, Y.-J. Chen, *Compos. Part Appl. Sci. Manuf.* **2015**, 68, 62.
- 696 [44] C.-M. Wu, M.-H. Chou, W.-Y. Zeng, *Nanomaterials* **2018**, 8, 420.
- 697 [45] S. Tiwari, A. Gaur, C. Kumar, P. Maiti, *Energy* **2019**, 171, 485.
- 698 [46] R. S. Sabry, A. D. Hussein, *Mater. Res. Express* **2019**, 6, 105549.
- 699 [47] S. Bairagi, S. W. Ali, *Eur. Polym. J.* **2019**, 116, 554.
- 700 [48] A. Mayeen, M. S. Kala, S. Sunija, D. Rouxel, R. N. Bhowmik, S. Thomas, N. Kalarikkal,
701 *J. Alloys Compd.* **2020**, 837, 155492.
- 702 [49] M. Abbasipour, R. Khajavi, A. A. Yousefi, M. E. Yazdanshenas, F. Razaghian, *J. Mater.*
703 *Sci. Mater. Electron.* **2017**, 28, 15942.
- 704 [50] Ö. F. Ünsal, Y. Altın, A. Çelik Bedeloğlu, *J. Appl. Polym. Sci.* **2020**, 137, 48517.
- 705 [51] M. Pusty, P. M. Shirage, *J. Alloys Compd.* **2022**, 904, 164060.
- 706 [52] J. Yang, Y. Zhang, Y. Li, Z. Wang, W. Wang, Q. An, W. Tong, *Mater. Today Commun.*
707 **2021**, 26, 101629.
- 708 [53] S. K. Karan, D. Mandal, B. B. Khatua, *Nanoscale* **2015**, 7, 10655.
- 709 [54] A. Anand, D. Meena, K. K. Dey, M. C. Bhatnagar, *J. Polym. Res.* **2020**, 27, 358.
- 710 [55] K. Lau, Y. Liu, H. Chen, R. L. Withers, *Adv. Condens. Matter Phys.* **2013**, 2013, 1.

- 711 [56] M. Baniasadi, Z. Xu, S. Moreno, S. Daryadel, J. Cai, M. Naraghi, M. Minary-Jolandan,
712 *Polymer* **2017**, 118, 223.
- 713 [57] M. Spasova, N. Manolova, N. Markova, I. Rashkov, *Fibers Polym.* **2017**, 18, 649.
- 714 [58] M. Baniasadi, Z. Xu, J. Cai, S. Daryadel, M. Quevedo-Lopez, M. Naraghi, M. Minary-
715 Jolandan, *Polymer* **2017**, 127, 192.
- 716 [59] S. Mohamadi, N. Sharifi-Sanjani, *Fibers Polym.* **2016**, 17, 582.
- 717 [60] G. Zhong, R. Su, L. Zhang, K. Wang, Z. Li, H. Fong, L. Zhu, *Polymer* **2012**, 53, 4472.
- 718 [61] N. Moazeni, A. A. Merati, M. Latifi, M. Sadrajahani, S. Rouhani, *Polymer* **2018**, 134, 211.
- 719 [62] C. J. Angammana, S. H. Jayaram, *IEEE Trans. Ind. Appl.* **2011**, 47, 1109.
- 720 [63] J.-Y. Yin, C. Boaretti, A. Lorenzetti, A. Martucci, M. Roso, M. Modesti, *Nanomaterials*
721 **2022**, 12, 962.
- 722 [64] M. Satthiyaraju, T. Ramesh, *Mater. Res. Express* **2019**, 6, 105366.
- 723 [65] S. Gee, B. Johnson, A. L. Smith, *J. Membr. Sci.* **2018**, 563, 804.
- 724 [66] M. Zeyrek Ongun, S. Oguzlar, E. C. Doluel, U. Kartal, M. Yurddaskal, *J. Mater. Sci.*
725 *Mater. Electron.* **2020**, 31, 1960.
- 726 [67] R. S. Sabry, A. D. Hussein, *Polym. Test.* **2019**, 79, 106001.
- 727 [68] Y. Zhang, S. Jiang, Y. Yu, Y. Zeng, G. Zhang, Q. Zhang, J. He, *J. Appl. Polym. Sci.* **2012**,
728 125, E314.
- 729 [69] M. M. Abolhasani, *Compos. Sci. Technol.* **2017**, 8.
- 730 [70] J. Zhang, X. Wang, X. Chen, X. Xia, G. J. Weng, *Energy Convers. Manag.* **2022**, 269,
731 116121.
- 732 [71] S. Kaur, A. Kumar, A. L. Sharma, D. P. Singh, *J. Mater. Sci. Mater. Electron.* **2017**, 28,
733 8391.
- 734 [72] Z. He, F. Rault, A. Vishwakarma, E. Mohsenzadeh, F. Salaün, *Coatings* **2022**, 12, 1310.
- 735 [73] M. Satthiyaraju, T. Ramesh, *Arab. J. Sci. Eng.* **2019**, 44, 5697.
- 736 [74] Z. J. Krysiak, Ł. Kaniuk, S. Metwally, P. K. Szewczyk, E. A. Sroczyk, P. Peer, P. Lisiecka-
737 Graca, R. J. Bailey, E. Bilotti, U. Stachewicz, *ACS Appl. Bio Mater.* **2020**, 3, 7666.
- 738 [75] U. Stachewicz, P. K. Szewczyk, A. Kruk, A. H. Barber, A. Czyrska-Filemonowicz, *Mater.*
739 *Sci. Eng. C* **2019**, 95, 397.
- 740 [76] R. Liu, Q. Liu, D. He, G. Sun, Z. Li, Y. Zhu, *ACS Appl. Electron. Mater.* **2021**, 3, 1804.
- 741 [77] H. Sun, H. Tian, Y. Yang, D. Xie, Y.-C. Zhang, X. Liu, S. Ma, H.-M. Zhao, T.-L. Ren,
742 *Nanoscale* **2013**, 5, 6117.

743 [78] C. K. Jeong, K.-I. Park, J. Ryu, G.-T. Hwang, K. J. Lee, *Adv. Funct. Mater.* **2014**, 24,
744 2620.

745 [79] Piezo-response Force Microscopy (PFM), [https://web.nanosurf.com/piezo-response-](https://web.nanosurf.com/piezo-response-force-microscopy-pfm-0)
746 [force-microscopy-pfm-0](https://web.nanosurf.com/piezo-response-force-microscopy-pfm-0).

747

748