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Flexible piezoelectric energy harvester based on self-poled electroactive P(VDF-HFP)/(Fe₂O₃-PANI) composite film

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Fabricating a piezoelectric generator for harvesting mechanical energy is a recent development that has exhibited great potential to enhance the piezoelectric coefficient, stretchability, flexibility, and integrability in small-scale (*i.e.*, micro or nano) power supply and sensor systems for diverse applications. In this study, we report on the preparation of a copolymer composite P(VDF-HFP)/(Fe₂O₃-PANI) film, *i.e.*, ('hfp-f^e-pⁿ'), fabricated by incorporating ferric oxide (Fe₂O₃) and polyaniline (PANI) fillers with the host poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)] copolymer that yields more than 99% electroactive β - and γ -phase formation, where a traditional electrical poling treatment was avoided. The nucleation and enhancement in the piezoelectric phase (*i.e.*, β -phase) and the conversion of the degree of crystallinity (χ_c) in the P(VDF-HFP) copolymer are governed by the incorporation of these fillers, as revealed by the Attenuated total reflectance (ATR) and X-ray diffraction (XRD) analyses. Furthermore, the electrostatic interactions between the surface charges of Fe₂O₃ and the interfacial dipole-dipole interaction of the (=N-H)⁺ group of PANI fillers with -CH₂-/-CF₂- molecular dipoles in P(VDF-HFP) cooperate to stabilize the electro-active phases and enhance its piezoelectric properties. A piezoelectric generator (PEG) fabricated with the 'hfp-f^e-pⁿ' film shows an open circuit voltage output of ~8 V and an output power of 10.3 nW. In addition, it generates enough power to instantly turn on commercial white/red light-emitting diodes (LEDs). The capacitor-charging capability of the PEG indicates its suitability for effectively harvesting mechanical energy from finger impact (a pressure amplitude of ~14 kPa) and as an alternative in the area of self-powered energy harvesting devices.

KEYWORDS

β -phase, piezoelectricity, P(VDF-HFP), Fe₂O₃, PANI

1 Introduction

With the development of scientific technology and energy limitations, renewable energy sources have become one of the most rapidly growing research areas. Traditionally, batteries are used as the primary energy source to power vast number of small electronic devices such as actuators, sensors, wireless transmitters, and other embedded systems in medical, remote-control, and environmental protection applications. However, with a limited lifetime, managing, monitoring, and recycling large quantities of batteries is a challenge. The waste of hazardous chemicals left in the exhausted batteries has become another crucial environmental threat. Each device requires only small-scale power, with an average of microwatt (μW) to milliwatt (mW) levels. As a result, developing self-powered system becomes an ideal approach to relieve energy crises and environmental threats (Chu and Majumdar, 2012; Fan et al., 2016). Therefore, a different energy harvesting method called 'nanogenerator' (NG) was introduced by Wang and Song in 2006 to symbolize the energy harvesting devices that generate electricity based on the piezoelectric effect from nanoscale piezoelectric materials by employing them in low-frequency mechanical vibrations accessible under ambient atmospheres and human body motions (Wang, 2006; Wang, 2017). In the last 10 years, different types of NGs, including piezoelectric nanogenerators (PENGs), triboelectric nanogenerators (TENGs), pyroelectric nanogenerators (PyNGs), and thermoelectric devices, have exhibited excellent performance in harvesting and converting energy from natural resources (Fan et al., 2012; Zi and Wang, 2017; Garain et al., 2015; Adhikary and Mandal, 2017). Among the various energy harvesting systems, converting mechanical energy into electric power is a recent emerging technology in self-powered electronic devices. Mechanical energy is one of the most abundant forms of energy in the environment; energy from walking, running, talking, using transportation, the motion of eyes, muscle stimulation, and even the movement of bodily fluids, heartbeats, and respiration is often wasted (Chu and Majumdar, 2012; Adhikary and Mandal, 2017). For self-powering Internet of Things (IoT) systems, this energy can be collected and used as an essential source of renewable energy. Therefore, unlike other energy converting systems, converting wasted mechanical energy into electricity has become one of the crucial technologies compared to TENGs and PyNGs in embedded electronic systems, biomedical sensor fabrication, and self-powering IoTs where the external power sources may be ignored (Garain et al., 2015; Zi and Wang, 2017). Several research groups have attempted to fabricate high-performance piezoelectric generators (PEGs) with well-grown nanostructures of inorganic piezoelectric materials, *i.e.*, BaTiO_3 , PZT, ZnSnO_3 , ZnO , and GaN , and their composite forms with polymers (Chen et al., 2010; Lin et al., 2012; Anand et al., 2020). Piezoelectric polymers, particularly poly(vinylidene fluoride) (PVDF) and its copolymers such as poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) and poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)), in their all-trans pseudohexagonal phase, offer recognizable advantages over ceramics in specific applications. These advantages include ease of processing at low temperatures, low density, low stiffness, flexibility, and mechanical robustness, such as toughness and the ability to withstand high strains before failure (Wu et al., 2022; Hoque et al., 2017; Singh et al., 2017; Saxena and Shukla, 2021; Nalwa and

Dekker, 1995). Recently, several investigations have revealed that the piezoelectric coefficient (d_{31}) and the electromechanical coupling factor (k_{31}) of P(VDF-HFP) (4.5 mol%) are significantly higher than those of PVDF and P(VDF-TrFE) copolymers. Moreover, the copolymer P(VDF-HFP) exhibits an unusual piezoelectric response, *i.e.*, $|d_{31}/d_{33}| > 1$, which is uncommon compared to other piezopolymers (Neese et al., 2007; Adhikary and Mandal, 2017). Owing to this property, P(VDF-HFP) might be responsible for longitudinal and transverse directions, making it more effective under ubiquitous environmental vibrations. P(VDF-HFP) has been reported as a ferroelectric copolymer having at least three regular conformations with similar energies; it occurs in several conformations: the α -phase (TGTG conformation) with alternating trans (T) and gauge (G) linkages; the β -phase (all *trans*, TTTT conformation); the semi-polar γ -phase (TTTG conformation); and the δ -phase (polarized α -phase), but only the β -, γ -, and δ -phases show favorable electroactivity specifically, piezoelectricity manifested through spontaneous polarization which is the focus of interest here. In contrast, among all of these phases, the α -phase is electrically inactive (Hoque et al., 2018; Shin et al., 2014; Chen et al., 2010; Chipara et al., 2020). It has been observed that the piezo-response and energy harvesting capability from the films arise due to molecular dipoles (*i.e.*, $-\text{CH}_2-/-\text{CF}_2-$) present in the P(VDF-HFP) copolymer matrix existing in the β -, γ -, and δ -phases and are directly related to and essentially proportional to effective polarization (Singh et al., 2017). So, enhancing the β -, γ -, and δ -phases will affect the piezoelectric response and the energy harvesting performances by increasing the number of external free electrons that accumulate on both sides of the composite films to balance the potential produced by the $-\text{CH}_2-/-\text{CF}_2$ dipoles (Hoque et al., 2018). Several techniques can be used to achieve the β - and γ -phases in P(VDF-HFP), including electrical poling, mechanical stretching, electrospinning, spin coating, and doping with different salt fillers and nanoparticles (Adhikary and Mandal, 2017; Sk et al., 2022). Particularly, it is widely accepted that mechanical stretching is required to achieve a polar electroactive β -phase that exhibits piezoelectricity after external electrical poling treatment (Mao et al., 2014). However, the stretched film suffers from surface and thickness inhomogeneity, which is unfavorable for device fabrication. In addition, electrical poling steps must be performed carefully as the film is susceptible to failure due to electrical breakdown. In addition, the great interest in wearable electronics increases the interest in self-powered technologies and continues to gain researchers' attention. Recently, piezoelectric composites with different fillers in a polymer matrix have emerged as promising candidates for PEGs and PENGs. These composites combine the high piezoelectric performance of the fillers with the flexibility of the polymer matrix. Examples include organic/inorganic piezoelectric composites such as BTO/PVDF, solid solution (BCZT)/PVDF, PZT/PVDF, and PZT/polydimethylsiloxane (PDMS) (Zhao et al., 2015). Sumanta *et al.* developed a flexible, sensitive, cost-effective hybrid piezoelectric nanogenerator (HPNG) by integrating flexible steel-woven fabric electrodes into a poly(vinylidene fluoride) (PVDF)/aluminum oxide-decorated reduced graphene oxide (AlO-rGO) nanocomposite film, where AlO-rGO acts as a nucleating agent for electroactive β -phase formation. The fabricated nanogenerator (HPNG) shows an unprecedented shifting of open-circuit output voltage to a high value of

~36 V and short-circuit current of ~0.8 μ A, corresponding to a power density of ~27.97 μ W/cm³ under repeating human finger imparting conditions, which are reported with PVDF-based PNGs (Karan et al., 2016). Yu et al. reported a high-performance β -PVDF-based piezoelectric and triboelectric hybrid nanogenerator (PTNG) employing large-scale PVDF films or bulks by using liquid nitrogen to induce the phase transition and *in situ* doped conductive polyaniline (PANI). Adding PANI as a conductive material opens the channel for carriers to move the charge in the bulk material. Subsequently, the polymer chains become entangled with each other through strong hydrogen bonding and dipole–dipole interactions. The PTNG exhibits excellent piezoelectric properties, and the optimal output of the PTNG, with a β -phase content of up to 71%, reaches 246 V and 122 μ A at a frequency of 30 Hz and a pressure of 0.31 MPa, and the power density is calculated to be 6.69 W/m² (Yu et al., 2021). Ongun et al. demonstrated electrospinning PVDF-based nanogenerators with various concentrations of iron oxide (Fe₂O₃) nanoparticles (0.2, 0.4, 0.6, and 0.8 wt%). In a nanogenerator with piezoelectric properties, the output voltage of β -PVDF in the presence of 0.4 wt% of Fe₂O₃ NPs reaches up to 1.39 V (Ongun et al., 2020). Chen et al. reported a flexible hybrid NG based on an array of P(VDF-TrFE) nanowires with improved piezoelectric output voltage/current of approximately 4.0 V/65 nA. Likewise, another hybrid NG was designed, consisting of micro-patterned P(VDF-TrFE) with a thickness of approximately 7 μ m, acting as both pyroelectric and piezoelectric layers; graphene nanosheets and a PDMS-CNT composite served as the two electrodes of the nanogenerator. The structure diagram of the hybrid piezoelectric–PyNG and SEM images of PDMS-CNT composite and P(VDF-TrFE) were provided. The highly stretchable PyNGs generated output voltages ranging from 8 mV to 2.48 V (Chen et al., 2016). Yang et al. demonstrated a flexible hybrid energy harvesting cell consisting of piezoelectric and pyroelectric NGs and solar cells, which can be employed to individually or simultaneously harvest thermal, mechanical, and solar energies. The presented cell was fabricated using PVDF with a film thickness of approximately 110 μ m and a flexible array of ZnO nanowires of diameters of approximately 100 nm and poly(3-hexylthiophene) (P₃HT) film heterojunctions for scavenging solar energy. The PVDF film-based piezoelectric NG showed an output voltage and a current of (0.5 V/20 nA) when a compressive strain was applied to the NG (Yang et al., 2012). It is realized that incorporating different external fillers in a polymer matrix is one of the most cost-effective and industrially friendly approaches in large-scale PEG fabrication (Davis et al., 1978; Chen et al., 2007; Lei et al., 2024; Parangusan et al., 2021).

In this study, we selected P(VDF-HFP) as a host material and incorporated Fe₂O₃ and PANI fillers to investigate the cooperative effect of the surface charges from Fe₂O₃ and the presence of the (=N–H)⁺ group in PANI within the ‘hfp-f^e-pⁿ’ composite film. The goal was to efficiently reduce the heterogeneity between two different dielectric phases, induce the electro-active β - and γ -phases, and enhance the piezoelectric response. In contrast, electrical poling steps can be avoided if self-poled techniques are implemented, and thus, a cost-effective piezoelectric-based device becomes easier to fabricate. A concentration of 0.6 wt% of Fe₂O₃ and PANI fillers in the P(VDF-HFP)/Fe₂O₃–PANI composite film resulted in the formation of more than 99% electroactive phase (F_{EA}). A decrease

in the piezoelectric β -phase content in the composite indicates the formation of the δ -phase (α_p -phase). This δ -phase may have contributed to dipole moment in aligned molecular dipoles along with the β - and γ -phases, which shows higher piezo voltage for the ‘hfp-f^e-pⁿ’ composite containing a lower β -phase. The addition of PANI to this as a conductive material opens the channel for carriers to move charge in the bulk material, and subsequently, the polymer chains become entangled with each other through strong hydrogen bonding and dipole–dipole interactions. Freely mobile electrons in the conductive PANI can promote the movement of charge in the material through the conductive network formed between PANI and P(VDF-HFP), thus improving energy transfer efficiency. It can be observed from the morphology analysis of the ‘hfp-f^e-pⁿ’ composite that the dispersion of PANI in the P(VDF-HFP) copolymer matrix causes more agglomerations of particles in the composite. This particular composite’s morphology helps reduce the loss of the material’s unique properties needed for energy harvesting applications. Metal oxides, such as iron oxide (Fe₂O₃), can be suitable reinforcement candidates in P(VDF-HFP) to improve the energy harvesting properties of polymer composites. Fe₂O₃ can create defects and alter the materials’ electronic structure, making it more responsive to mechanical stress. It is also observed that ferric oxide (Fe₂O₃), when doped at concentrations above the critical threshold of 0.4 wt% of Fe₂O₃ NPs in PVDF, shows unusual behavior within the composite. Yempally et al. reported a simple and fast non-solvent-induced phase separation (NIPS) process to develop PVDF-based polymer composites containing Zn–Fe₂O₃ nanomaterials. At 3 wt%, Zn–Fe₂O₃ induced an open-circuit voltage of 0.41 V, which is approximately 12 times greater than that of the neat PVDF film (Yempally et al., 2023). We have mainly focused our study on the synergistic effects of Fe₂O₃ and PANI fillers in the P(VDF-HFP) copolymer matrix. The fabricated ‘hfp-f^e-pⁿ’-based flexible PEG’s output voltage response of ~8 V demonstrated the different electroactive phase formations in the copolymer matrix and the contributions of Fe₂O₃ and PANI fillers. The PANI filler effectively reduces the internal resistance of the PEG and easily forms a conduction pathway through its network structure, and Fe₂O₃ acts as a reinforcing agent in the P(VDF-HFP) copolymer matrix.

2 Experimental sections

2.1 Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) pellets ($M_w \sim 275,000$, Sigma-Aldrich, United States), N, N-dimethylformamide (DMF) (Merck Chemical, India), ferric oxide (Fe₂O₃) (Alfa Aesar), and polyaniline (PANI) (SRL, India) were used in the experiment.

2.2 Preparation of the composite film

We used a simple solution-casting method to prepare these films without mechanical, thermal, or electrical treatment. First, 6 wt% of P(VDF-HFP) was dissolved in 10 mL of DMF by continuous stirring for 12 h at 60°C. The solution was designated as the ‘hfp’ solution. Then, we divided the solution into five equal parts and

kept them in vials; one of the vials was used as the reference sample, referred to as the 'neat' sample. Then, the same amounts, *i.e.*, concentrations (0.2, 0.4, 0.6, and 0.8, 1 wt%), of Fe_2O_3 and PANI were added into the remaining vials containing the 'hfp' solution. The mixtures were vigorously stirred under constant magnetic stirring for 6 h to ensure proper dissolution of the external additives and homogeneous dispersion in the composite films. Afterward, the 'neat' and composite solutions were drop-cast onto the clean glass slides and dried at 60°C for 5 h. Finally, the resulting free-standing dried films were peeled off the glass substrates for further characterization and device fabrication. The films were designated as "hfp" for the neat, where the external additives were not added, and 'hfp-f^e', 'hfp-pⁿ' and 'hfp-f^e-pⁿ' for the composites. A thick film (thickness ~ 0.2 mm) of the 'hfp-f^e-pⁿ' sample was also prepared at 60°C for energy harvesting applications. For simplicity, we used the short notations of these external additives, *i.e.*, 'f^e' for ferric oxide (Fe_2O_3) 'pⁿ' for polyaniline (PANI).

2.3 Film characterization

The crystalline phases of the 'hfp' and 'hfp-f^e-pⁿ' films that are relevant to the characteristic vibrational modes of the molecular chain of copolymer P(VDF-HFP) were identified via attenuated total reflectance (ATR) spectroscopy. The ATR spectra were recorded on a Bruker Tensor II Spectrometer with a spectral resolution 4 cm^{-1} . An X-ray diffractometer (Empyrean, D8 ADVANCE) in the range $2\theta = 0^\circ$ – 100° with CuK_α radiation of $1.54\text{ \AA}$ wavelength was used to analyze the crystallographic information of the P(VDF-HFP) polymorph and its degree of crystallinity (χ_c). The surface morphology of the films was studied using a field emission scanning electron microscope (FE-SEM) (JEOL, JSM-IT100) operated at an accelerating voltage of 20 kV. The energy harvesting performances, such as the piezoelectric output by finger tapping, capacitor charging voltage data, and powering up of LEDs from the PEG through a typical bridge circuit, were recorded using a digital storage oscilloscope (DSO) and a normal digital multimeter, where we recorded the readings in a video, as presented in the results and discussion section. All measurements were carried out at room temperature.

3 Results and discussion

3.1 Characterizations of the composite film

3.1.1 Spectroscopic analysis

ATR spectroscopy of the films was performed to understand the crystalline phase identifications of the polymorphs regarding local phonon bands of P(VDF-HFP) and analyze the piezoelectric β -phase and electroactive γ -phase formation. Now, a piezoelectric material should have non-centro symmetry. In copolymer P(VDF-HFP), α -, β -, γ -, δ -, and ϵ - are the five well-known phases of molecular chain conformation, and among them, the β -phase is polar-electroactive and ferroelectric and is responsible for the piezo- and pyroelectric properties of the material. In the ATR spectra (Figure 1a), the characteristic phonon modes of the well-known phases provide clear insights into the development of the

different phases of the films, and the spectra confirm the presence of a predominantly non-electroactive α -phase in the 'hfp' and 'hfp-f^e' film, which is evidenced by characteristic vibrational bands at 616 and 764 (CF_2 bending and skeletal bending), 797 (CH_2 rocking), 978, and $1,211\text{ cm}^{-1}$, along with a trace amount of β/γ -phases revealed by the presence of a weak band at 840 cm^{-1} (CH_2 rocking) (Martins et al., 2014; Maity et al., 2018). After the two fillers, Fe_2O_3 and PANI, were introduced into the 'hfp' solution, prominent characteristic peaks at $1,233\text{ cm}^{-1}$ ($\delta(\text{CH}_2) + \omega(\text{CH}_2)$) and $1,277\text{ cm}^{-1}$ (trans band) ($\nu_s(\text{CF}_2) - \nu_s(\text{CC}) + \delta(\text{CCC})$) appeared in the composite 'hfp-pⁿ' and 'hfp-f^e-pⁿ' films, which represent the piezo-, pyro-, and ferroelectric properties of the films with the formation of the characteristic bands of the electro-active γ - and β -phases in the doped samples, and all α -phase characteristic bands are completely diminished, as also shown in Figure 1a (Adhikary and Mandal, 2017; Sk et al., 2022). Apart from this, the presence of the 764 and $1,277\text{ cm}^{-1}$ peaks is indicative of the α - and β -phases, respectively. The intense peak at 840 cm^{-1} ($r(\text{CH}_2) - \nu_s(\text{CF}_2)$) also indicates the presence of both the β - and γ -phases, which exhibit similar local structures, and these phases resemble each other structurally and spectroscopically due to their shared 'TTT' molecular chain conformation and common phonon bands (Singh et al., 2017; Greijer et al., 2022). The $\omega(\text{CH}_2)$ mode coupled with $\nu_{as}(\text{CC})$ is responsible for the main intense band that arises at $1,401\text{ cm}^{-1}$, whereas $\nu_{as}(\text{CF}_2)$ linked with the $\rho(\text{CF}_2)$ and $\rho(\text{CH}_2)$ vibrational modes, respectively, are responsible for those at 1,180 and 877 cm^{-1} . The skeletal vibrations of the P(VDF-HFP) co-polymer are mostly represented by these bands, and the intensity of the β -phase ($1,277\text{ cm}^{-1}$) is consistently observed to be lower than that of the skeletal vibrational bands that originate from the backbone structure. These bands are very useful for evaluating the effect of $-\text{CH}_2-/-\text{CF}_2-$ dipoles (which are responsible for the piezo-response and energy harvesting performances) of the P(VDF-HFP) copolymer in the investigated films. Thus, the external fillers Fe_2O_3 and PANI used in the 'hfp' solution play a significant role in the crystallographic phase transformation (*i.e.*, $\alpha \rightarrow \gamma/\beta$ phase) by stretching the copolymer P(VDF-HFP) configuration along its backbone, thereby polarizing the net electric dipole, and in the stabilization and improvement of the electroactive phases in P(VDF-HFP), which mainly contain β - and γ -phases. This is evidenced by the appearance of two characteristic bands at $1,277\text{ cm}^{-1}$ (β -phase) and $1,233\text{ cm}^{-1}$ (γ -phase), as observed in the 'hfp-f^e-pⁿ' composite film. We also studied the optimal concentration of Fe_2O_3 and PANI fillers in the 'hfp-f^e-pⁿ' composite film and found that a concentration of 0.6 wt% for each filler results in the formation of more than 99% electroactive phases (F_{EA}). We carried out ATR spectroscopy on the composite films with different concentrations of Fe_2O_3 and PANI fillers (0.2, 0.4, 0.8, and 1 wt%) to identify the optimal composition for maximizing the output of the PEG, and the corresponding percentage (%) of electro-active phases in each sample was also evaluated. The corresponding results are provided in ESI† (Supplementary Figure S1). The difference in activity to promote electro-active phases' nucleation in P(VDF-HFP) is due to the difference in the size and surface morphology of the two fillers (Thakur et al., 2015). So, for the nucleation of the piezoelectric β -phase, the above mentioned ATR bands are very useful for examining the interaction between different molecules and evaluating the effect of the fillers Fe_2O_3 and PANI on the locally

oriented packing of $-\text{CH}_2-/-\text{CF}_2-$ dipoles of the P(VDF-HFP) copolymer chain, which is oriented in the all-trans ‘TTTT’ molecular conformation in the external filler-added ‘hfp’ film. To represent the presence of both β - and γ -phases simultaneously, the intensity of absorption of the 840 cm^{-1} band is selected for the calculation of F_{EA} , i.e., the percentage of the electro-active phase in the sample. F_{EA} can be calculated using Equation 1 as follows:

$$F_{EA} = \frac{A_{EA}}{\left(\frac{K_{840}}{K_{764}}\right) \times A_{NEA} + A_{EA}} \times 100\%, \quad (1)$$

where A_{EA} is the intensity of absorbance at 840 cm^{-1} , A_{NEA} is the intensity of absorbance at 764 cm^{-1} , K_{840} is the coefficient of absorption at wave number 840 cm^{-1} , and K_{764} is the coefficient of absorption at wave number 764 cm^{-1} . $K_{840} = 7.7 \times 10^4\text{ cm}^2\text{mol}^{-1}$, and $K_{764} = 6.1 \times 10^4\text{ cm}^2\text{mol}^{-1}$. The normalization of ATR absorption was carried out with respect to the $1,070\text{ cm}^{-1}$ band (related to the thickness of composite films) before quantitative estimation of the relative amount of polar and nonpolar phase fractions. To separate β - and γ -phases at 840 cm^{-1} and to quantify them individually, we have deconvoluted the ATR spectra of the ‘hfp’ and ‘hfp-f^e-pⁿ’ films in the range from 720 to 930 cm^{-1} , as shown in Figure 1d, where the ATR pattern of the 840 cm^{-1} band was isolated by the Gaussian function for calculating the relative proportion of individual electroactive β -, i.e., $F(\beta)$, and γ -, i.e., $F(\gamma)$, phases, separately. The relative proportion of individual β - and γ -phases is calculated using Equations 2a, b as follows:

$$F(\beta) = F_{EA} \times \frac{A_{\beta}}{A_{\beta} + A_{\gamma}} \times 100\%, \quad (2a)$$

and

$$F(\gamma) = F_{EA} \times \frac{A_{\gamma}}{A_{\beta} + A_{\gamma}} \times 100\%, \quad (2b)$$

where A_{β} and A_{γ} represent areas of the band under the deconvoluted curves of the β - and γ -phases, respectively, which are centered at 840 cm^{-1} .

The deconvoluted curve centered at 840 cm^{-1} of the ‘hfp’ and composite ‘hfp-f^e’, ‘hfp-pⁿ’ and ‘hfp-f^e-pⁿ’ films are represented in Figure 2. Using Equations 2a, b, the proportions of β -, i.e., $F(\beta)$, and γ -, i.e., $F(\gamma)$, fractions are found to be 75% and 23%, respectively, for the ‘hfp-f^e-pⁿ’ composite. It should be noted that there is a decrease in the β -phase content ratio in the composite. This is due to the growth of a polarized α -phase that exhibits properties analogous to electroactive phases, such as the β -phase; in other words, the formation of δ -phase may occur in the composite during film preparation. For the other composites, the calculated values of $F(\beta)$ and $F(\gamma)$ are tabulated in Table 1. So, using 0.6 wt% of both Fe_2O_3 and PANI fillers in the copolymer P(VDF-HFP) results in a higher yield of electroactive phases, which might be more suitable for designing piezo-, pyro-, and ferroelectric-based sensors, actuators, and vibration-based energy harvesters.

The ATR spectra in the frequency region $3,150$ – $2,850\text{ cm}^{-1}$ of the ‘hfp’ and ‘hfp-f^e-pⁿ’ films of the $-\text{CH}_2-$ asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations are shown in Figure 1b, where clear shifting, as indicated by arrows, is observed in the ‘hfp-f^e-pⁿ’ film compared to the ‘hfp’ film, which is strong indication of

the interfacial interaction that is caused by the negative surface charges of the Fe_2O_3 filler and the positive $-\text{CH}_2$ dipoles present in the P(VDF-HFP) copolymer matrix that will damp the vibration of CH_2 molecules because the effective mass will increase. We have also compared the ATR spectra in the frequency region $3,150$ – $2,850\text{ cm}^{-1}$ of the ‘hfp’ and ‘hfp-f^e’ films, where clear shifting, as indicated in ESI† (Supplementary Figure S2), is observed in the ‘hfp-f^e’ composite, which is a clear indication of the interfacial interaction that is caused by the negative surface charges of the Fe_2O_3 filler and $-\text{CH}_2$ dipoles present in the P(VDF-HFP) matrix. So, it is observed that in the ‘hfp-f^e-pⁿ’ composite, filler Fe_2O_3 stretches the molecular configuration of the P(VDF-HFP) copolymer and acts as a damping source for oscillations of the $-\text{CH}_2$ dipoles of concomitantly lower energy of the (ν_{CH_2}) vibrations, resulting in stabilized longer TTTT or all-*trans* conformation on the surfaces of the Fe_2O_3 filler (Figure 1c). Nucleation of the β -phase also takes place through interfacial dipole–dipole interactions and has been found to have more influence on the phase transformation of P(VDF-HFP) due to the stronger interaction. In the case of the PANI filler, the $-\text{CF}_2$ dipoles of P(VDF-HFP) and the $(=\text{N}-\text{H})^+$ group of PANI also stimulate the interfacial dipole–dipole interaction, which drives the self-polarized $-\text{CH}_2-/-\text{CF}_2-$ dipoles in a unidirectional orientation for the higher yield of piezoelectric β -phase formation (Figure 1c).

3.1.2 X-ray diffraction studies

P(VDF-HFP) is semi-crystalline and approximately 50% amorphous with several stable crystalline forms. The piezoelectric performance of P(VDF-HFP) depends on the electroactive crystalline phases’ content, where the β -phase is the most piezoelectrically responsive one. The XRD pattern, as shown in Figures 3a, b, of the ‘neat hfp’ and ‘hfp-f^e’ films shows peaks at 17.6° (100), 18.3° (202), 19.8° (110), and 19.9° (110) of the diffracting planes that are attributed to the presence of the characteristic non-electroactive α -phase (Benz and Euler, 2003; Jin et al., 2013; Chen et al., 2007). On the other hand, Figures 3c, d show that the fillers Fe_2O_3 and PANI used in the ‘neat hfp’ sample, i.e., ‘hfp-pⁿ’ and ‘hfp-f^e-pⁿ’ films, possess an intense diffraction 2θ peak as a doublet at 20.6° of two overlapping lattice reflections of the diffracting planes (110)/(200) due to the presence of the piezoelectric polar β -phase along with a trace amount of moderately polar γ -phase, which is confirmed by the presence of three additional peaks (202), (110), and (110) at 18.5° , 20.4° , and 20.2° , respectively (Adhikary et al., 2016; Martins et al., 2014; Gregorio, 2006; Chen et al., 2021). So, the XRD results reveal that electroactive β - and γ -phases are formed in these composite films, and α -characteristic peaks still exist in the ‘hfp-f^e’ film. It may be due to the growth of polarized α -phase, i.e., the formation of δ -phase (α_p -phase) in the composite ‘hfp-f^e’ film during film preparation, which is also clear from the ATR spectrum with a dominant peak at 764 cm^{-1} , the characteristic peak of the α -phase. Among the different phases of the polymer PVDF, the δ -phase is analogous to the polarized form of the α -phase, also known as the α_p -phase, which is electroactive, and few recent studies also showed that the δ -phase has almost analogous electroactive properties like the piezoelectric β -phase (Mishra et al., 2022; Gupta et al., 2021; Martin et al., 2017; Chipara et al., 2020). The peak intensity with the addition of external fillers at these doublet 2θ values is enhanced due to the interaction between

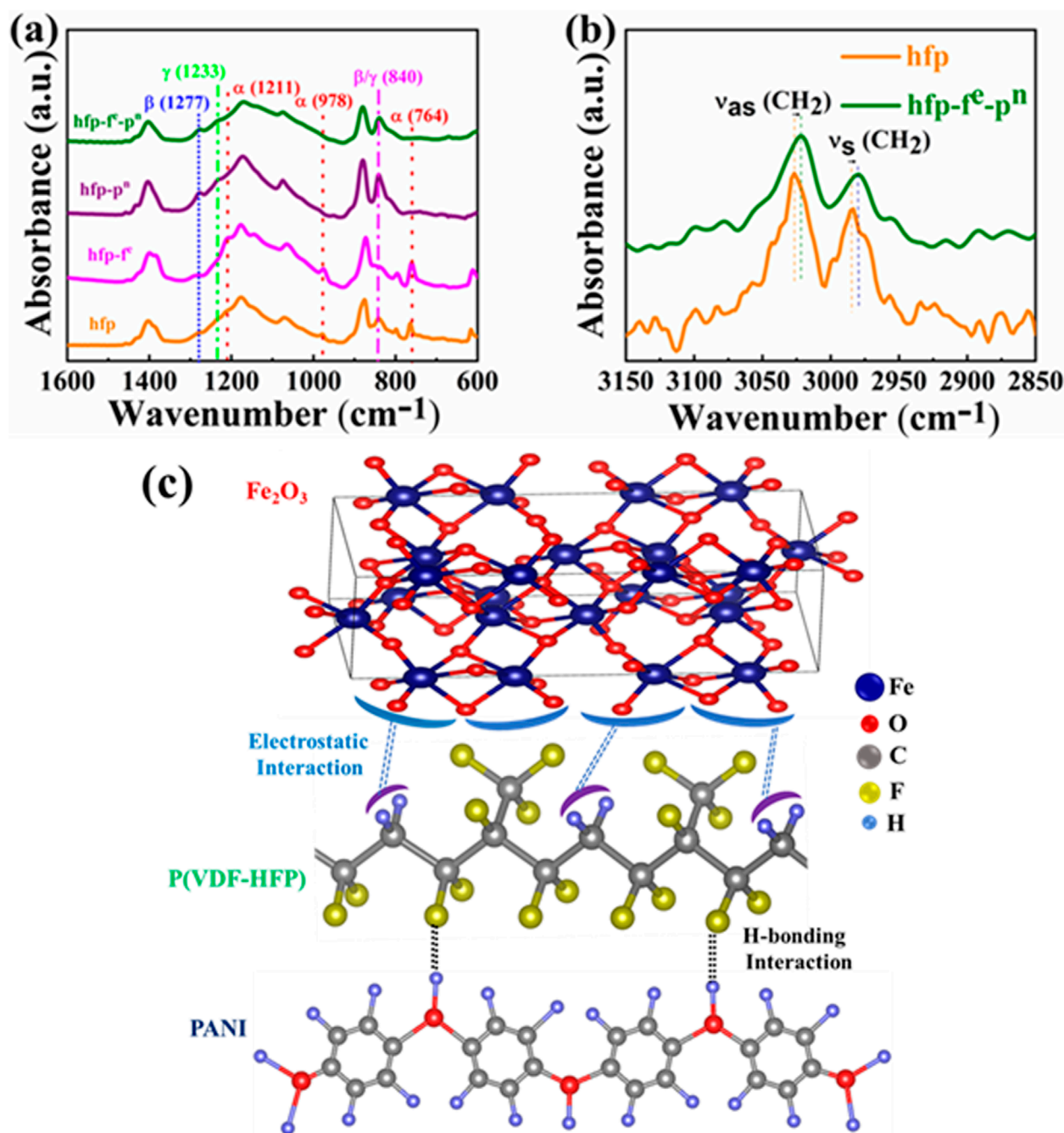


FIGURE 1

(a) ATR spectra of 'hfp' film and 'hfp-f^e', 'hfp-pⁿ' and 'hfp-f^e-pⁿ' composite films in the range from 1,600 to 600 cm⁻¹. (b) An enlarged view from 3,150 to 2,850 cm⁻¹ of the ATR spectra demonstrates the frequency shifting of the (–CH₂–) stretching vibrations. (c) Plausible interaction mechanism between Fe₂O₃/PANI and P(VDF-HFP) molecular chains, inducing the formation of the TTTT conformation.

the –CH₂–/–CF₂– dipoles of P(VDF-HFP) and the fillers at the interfaces, inducing the formation of a greater amount of crystalline β-phase in the composite 'hfp-pⁿ' and 'hfp-f^e-pⁿ' films than in the pure 'hfp' and 'hfp-f^e' films. Thus, all α-phase characteristic peaks are transformed (*i.e.*, α → γ/β phase) in the 'hfp-f^e-pⁿ' film as fillers Fe₂O₃ and PANI play important roles in inducing a crystallographic α → γ/β phase transformation in the P(VDF-HFP) matrix, which is confirmed further with the ATR spectroscopic data analysis. It is

noteworthy that the broad peak at 20.5° arises from the overlapping of β-phase peak [at 20.6° (110)/(200)] and γ-phase peak [at 20.4° (110)]. So, curve deconvolution of the peak at 20.5° can provide information on the crystallites of β- and γ-phases. The broad halo around these intense doublet 2θ peaks arises from the amorphous components of the P(VDF-HFP) copolymer. So, the crystalline and amorphous regions shown in the XRD patterns were isolated first by the Gaussian function to calculate the average degree of total

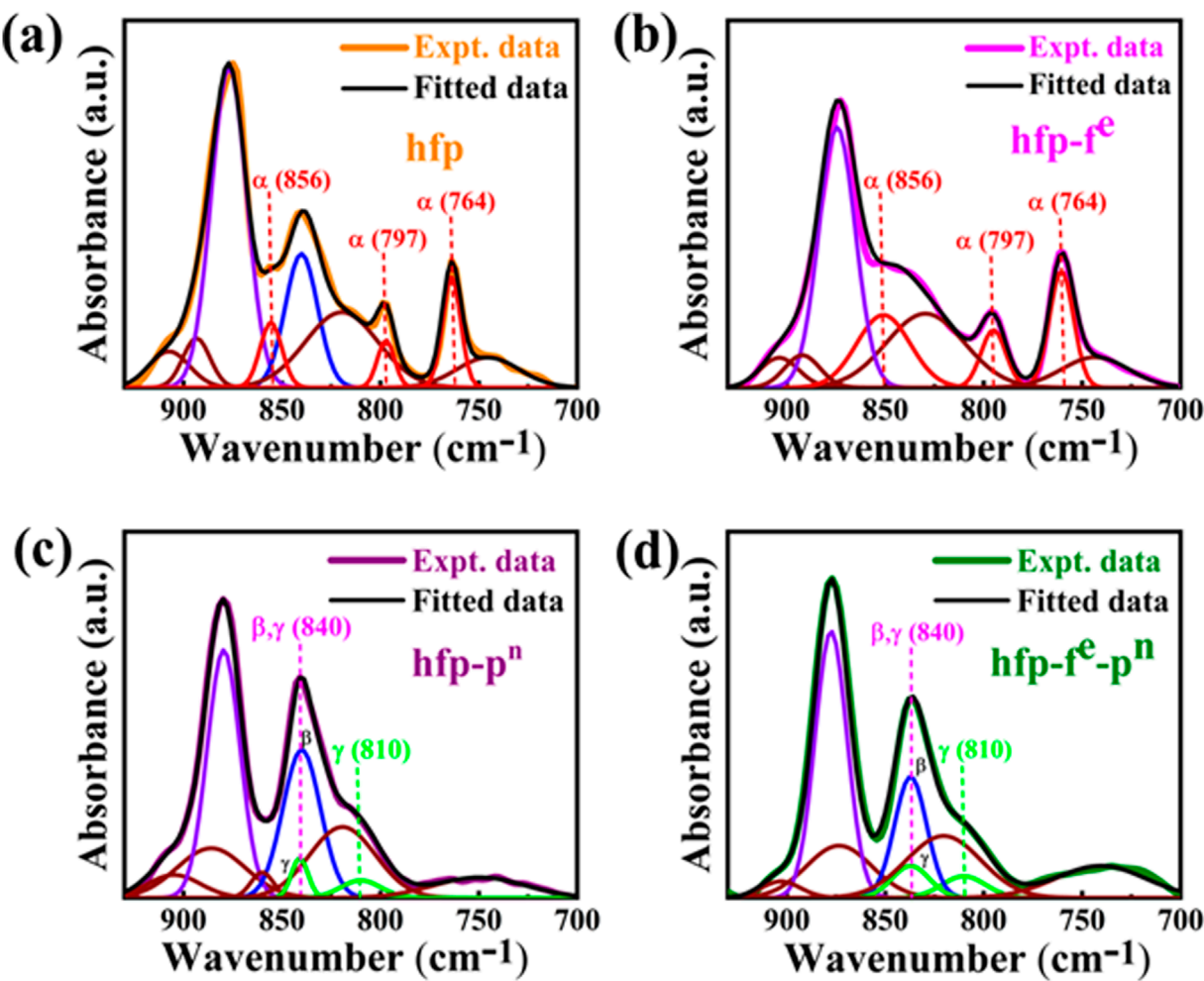


FIGURE 2 ATR spectra for (a) ‘hfp’ film and (b) ‘hfp-f^e’, (c) ‘hfp-pⁿ’ and (d) ‘hfp-f^e-pⁿ’ composite films that are deconvoluted in the region from 720 to 930 cm⁻¹ to identify β- and γ-phases present at 840 cm⁻¹.

TABLE 1 The degree of crystallinity in percentage (%) and the sizes of the films’ α-, β-, and γ-crystallites determined by ATR and XRD spectra.

Film	F(β) (%)	F(γ) (%)	χ _c (%)	χ _β (%)	χ _γ (%)	t _α (×10 ⁻¹⁰ m)	t _β (×10 ⁻¹⁰ m)	t _γ (×10 ⁻¹⁰ m)
hfp	—	—	44	—	—	0.9	—	—
hfp-f ^e	—	—	39	—	—	0.9	—	—
hfp-p ⁿ	84	10	37	31	4	—	0.9	0.8
hfp-f ^e -p ⁿ	75	23	34	25	7	—	0.8	0.6

crystallinity (χ_c) using Equation 3 as follows:

$$\chi_c = \frac{\sum A_{cr}}{\sum A_{cr} + \sum A_{amr}} \times 100\%, \tag{3}$$

where $\sum A_{cr}$ and $\sum A_{amr}$ represent the total integrated areas due to the crystalline diffraction peaks and amorphous halos. Overall crystallinity (χ_c) in the ‘neat hfp’ sample is found to be 44%. The

average size of the α-, β-, and γ-crystallites was estimated using the Debye–Scherrer formula presented in Equation 4 and tabulated in Table 1.

$$t = \frac{k\lambda}{B \cos \theta}, \tag{4}$$

where ‘t’ is the crystallite size, ‘B’ is the full width at half maximum (FWHM) of the diffraction peak in radians, ‘λ’ is the

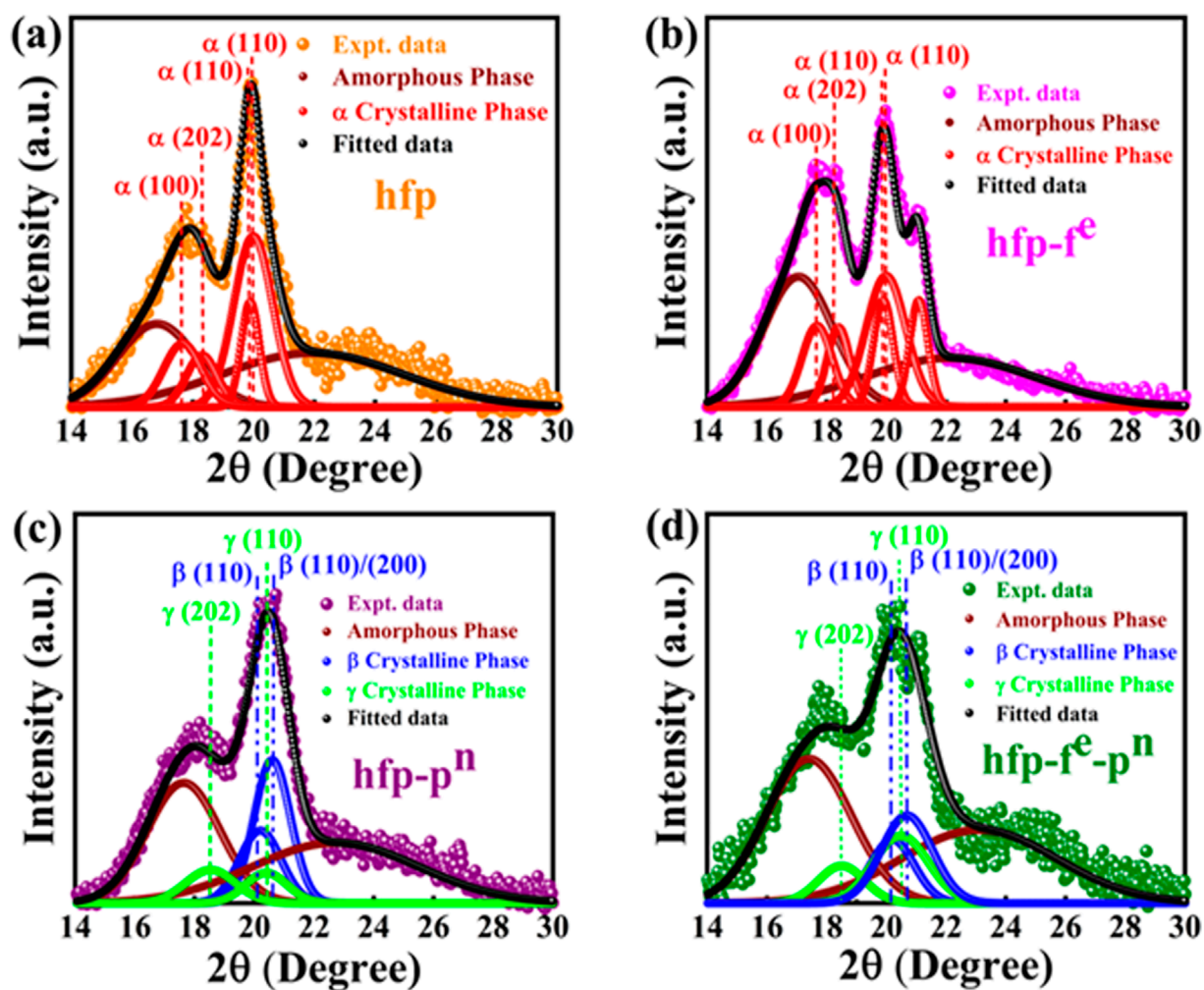


FIGURE 3
XRD patterns for (a) 'hfp' film and (b) 'hfp-f^e', (c) 'hfp-pⁿ' and (d) 'hfp-f^e-pⁿ' composite films deconvoluted in the 14°–30° range.

X-ray wavelength (*i.e.*, 1.54 Å), and $k = 0.89$ is a constant. The individual degree of crystallinity of the respective crystalline, *i.e.*, β - and γ -phases, can be calculated using Equations 5a, b, which are tabulated in Table 1.

$$\chi_{\beta}(\%) = F(\beta) \times \chi_C(\%), \quad (5a)$$

and

$$\chi_{\gamma}(\%) = F(\gamma) \times \chi_C(\%). \quad (5b)$$

It should be noted that in the 'hfp-f^e-pⁿ' film with added fillers Fe₂O₃ and PANI, the initial value of the 'hfp' film ($\chi_C = 44\%$) is reduced to 34%, as shown in Table 1. It is a common characteristic of reinforced polymer composite films, which are well-suited for improving dielectric properties.^{7,8,18} In addition, the fillers act as physical obstacles that may block the segmental motions and further stabilize the local phonons of the copolymer's molecular chain that possess the registration of all-trans conformations, which consequently function as nucleation sites to improve the crystallite size and the content of the

polar piezoelectric β -phase formation. Since the piezo-response is directly related to β -crystallinity, 0.6 wt% 'hfp-f^e-pⁿ' composite film is expected to exhibit a greater piezo-response, making it a strong candidate for the fabrication of mechanical energy harvesters.

3.1.3 Morphological study

For crystalline phase identification, surface morphology is one of the important parameters for the P(VDF-HFP) copolymer as most of the characteristics of the materials depend on their surface morphology (Garain et al., 2015; Adhikary and Mandal, 2017). The FE-SEM image shown in Figure 4a of the film shows the presence of a predominant α -phase, evidenced by the spherulitic texture of the micrometer scale, one of the characteristic features of α -phase presence that are consistent with the ATR and XRD data. Fe₂O₃ and PANI fillers utilized in P(VDF-HFP) give rise to polymer microstructures, as observed by the surface morphology (Figure 4b) of the composite 'hfp-f^e-pⁿ' film. The presence of Fe₂O₃ and PANI on the surface of the 'hfp-f^e-pⁿ' composite film sample was confirmed by EDS spectra at each of the locations

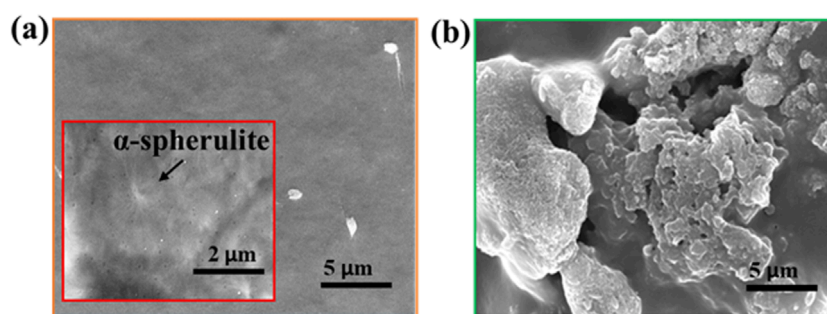


FIGURE 4
Surface morphology of the (a) 'hfp' and (b) 'hfp-f^e-pⁿ' films. The inset of (a) shows a high-magnification FE-SEM image of the 'hfp' film to show the characteristic spherulitic texture of the α -phase.

investigated, as shown in [Supplementary Figure S4](#). As observed in the FE-SEM images, incorporating fillers into the P(VDF-HFP) matrix leads to some morphological alterations. A large number of aggregated particles likely consisting of indistinguishable Fe_2O_3 and agglomerate PANI fillers are observed on the surface of the modified copolymer matrix, *i.e.*, in the 'hfp-f^e-pⁿ' film. This agglomeration is likely due to the formation of the polymer-filler complexes through interactions with the charges of different fillers, resulting in their non-uniform distribution within the modified co-polymer matrix ([Thakur et al., 2015](#); [Jisha et al., 2020](#); [Yempally et al., 2023](#)). It should also be noted that in the modified 'hfp-f^e-pⁿ' film, the stability of the copolymer and its miscibility can be promoted by dipole or van der Waals interactions. The composite is miscible due to the dipole/dipole interactions between the $-\text{CF}_2$ groups of P(VDF-HFP) and the $(=\text{N}-\text{H})^+$ groups of PANI and the interfacial interactions by the negative surface charges of Fe_2O_3 and $-\text{CH}_2$ dipoles present in the P(VDF-HFP) matrix. These types of interactions have the potential to create novel morphologies and alter the spherulitic morphologies of P(VDF-HFP), respectively. The clustering of PANI and Fe_2O_3 results from enhanced interfacial interaction among the constituent fillers, which can be attributed to the compatibility between the fillers and the P(VDF-HFP) copolymer matrix. The morphology of this particular composite will help in reducing the dielectric loss of the material. So, in the 'hfp-f^e-pⁿ' film, where external fillers are incorporated into the 'neat hfp' sample, the characteristic spherulitic texture of the α -phase is significantly reduced. This signifies that fillers can hinder the growth of the non-electroactive α -phase and promote the formation of the electroactive phases, *i.e.*, β - and γ -phases ([Adhikary and Mandal, 2017](#); [Sk et al., 2022](#); [Adhikary et al., 2015](#)). Thus, it is expected that the refined microstructure of the host P(VDF-HFP) copolymer created by introducing the Fe_2O_3 and PANI fillers might play an obvious role in promoting the piezoelectric response and the energy harvesting performances in a synthesized 'hfp-f^e-pⁿ' composite film.

3.1.4 Energy harvesting performances

To fabricate the flexible PEG, the different films of thickness $0.2 \text{ mm} \pm 9 \mu\text{m}$ with an area of $3 \times 1 \text{ cm}^2$ were placed between two aluminum foil electrodes. The entire multilayer structure was

then carefully encapsulated using polydimethylsiloxane (PDMS) (SYLGARD 184 Silicone Elastomer) adhesive, prepared with a 10:1 ratio of base to curing agent, and cured in an oven at 60°C for 30 min; this encapsulation ensured structural compactness and provided protection against physical damage. The final cured thickness of the PDMS layer is approximately $42 \mu\text{m}$ on either side of the electrode-polymer-electrode (EPE) stack, and the corresponding schematic is presented in [Figure 6a](#). The piezo-potential was measured using a DSO using repetitive stress by constant finger tapping applied on the surface of the PEGs of the films, which causes the creation of net dipole moment of $-\text{CH}_2-/-\text{CF}_2-$ dipoles present in the P(VDF-HFP) matrix. The piezo-response was measured without applying any electrical poling treatment, which is essential for dipole alignment. Here, it can be assumed that the behavior of the dipoles in copolymer P(VDF-HFP) is self-polarized in a specific direction that helps induce polarization, *i.e.*, resulting in the piezoelectric β -phase formation. Theoretically, it is also observed that piezoelectricity is directly related to and essentially proportional to effective polarization ([Mahapatra et al., 2021](#)). So, contributing to microstructural studies of the films can play a significant role in understanding the mechanism better. At the initial state, *i.e.*, before any finger impact on these PEGs' surface, no electric output is observed because no charge transfer occurs through the external circuit. This is due to the absence of a change in the dipole moment of the aligned molecular dipoles, *i.e.*, $-\text{CH}_2-/-\text{CF}_2-$ present in the P(VDF-HFP) matrix existing in the β -phase. When a compressive force is applied by the finger, the surface of the PEG experiences vertical strain, leading to deformation of the β -crystalline structure in the composite films, which causes a piezo-response; in other words, electric output is observed because of charge transfer through the external circuit ([Singh et al., 2017](#); [Maity et al., 2018](#)). [Figure 5](#) shows the piezoelectric output voltage responses of the 'hfp' film and 'hfp-f^e', 'hfp-pⁿ', and 'hfp-f^e-pⁿ' composite films by applying external mechanical pressure from constant finger tapping on the PEG's surface (impact pressure amplitude of $\sim 14 \text{ kPa}$, directly measured using a Flexi Force sensor (A201)). It shows a higher open-circuit voltage of $\sim 8 \text{ V}$ in the 'hfp-f^e-pⁿ' composite film (PEG) than that in other PEGs, as shown in [Table 2](#). To ensure that the output voltage mainly originated from the piezoelectric effect, we have checked the

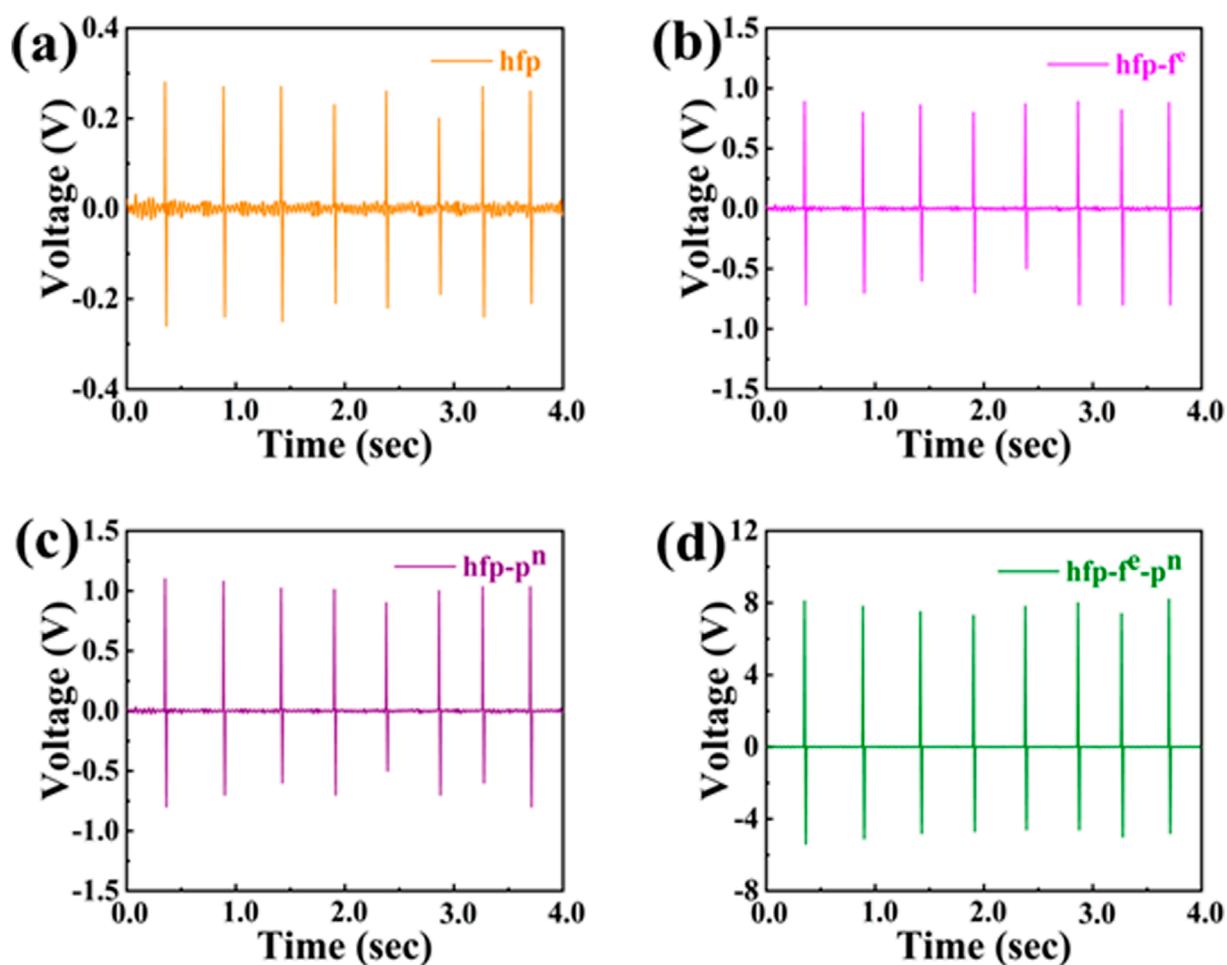


FIGURE 5
Non-rectified finger touch response from the PEGs prepared with (a) 'hfp,' (b) 'hfp-f^e,' (c) 'hfp-pⁿ,' and (d) 'hfp-f^e-pⁿ' films.

finger touch response of the 'hfp-f^e-pⁿ' PEG in both forward and reverse connections, as shown in ESI† (Supplementary Figure S5). When the finger was in contact with the upper surface of the PEG, a piezoelectric potential difference occurred through the electrodes via compressive force, and it gave rise to a positive output voltage, *i.e.*, the 'touch' response. After the pressure was released from the upper surface of the PEG, the composite film tried to return to its unstressed state, resulting in a voltage impulse with reversed polarity, which was assigned as the 'release' response.

So, it should be noted that the piezo-response in the 'hfp-f^e-pⁿ' composite film arises solely from the reversible transformation of the overall deformed β -crystalline structures of $-\text{CH}_2-/-\text{CF}_2-$ dipole present in the P(VDF-HFP) copolymer matrix into more stable configurations and *vice versa* under the application of external pressure. The charges generated by the external additives Fe_2O_3 and PANI utilized in the 'hfp' solution actively interact with the $-\text{CH}_2-/-\text{CF}_2-$ dipoles of P(VDF-HFP) for the nucleation of the piezoelectric β -phase by filler-induced polarization, resulting in self-polarized films under local stress development and propagation over the joint structures (Sk et al., 2022; Adhikary et al., 2015). To gain

better understanding with the applied pressure, a spontaneously induced distortion, *i.e.*, a change in the object's shape, size, or position, in the fillers Fe_2O_3 and PANI causes marked improvement in the piezoelectric response by the interplay of the sample between its initial and final states (Lei et al., 2024; Parangusan et al., 2021). On the other hand, the electrical potential generated by the applied external pressure further facilitates the alignment of $-\text{CH}_2-/-\text{CF}_2-$ electric dipoles in a unidirectional manner via stress-induced polarization. The piezoelectricity arising in the PEG fabricated with an electro-active phase that dominated the 'hfp-f^e-pⁿ' film is mainly due to the combined effect of the change in the dipole moment by the applied external mechanical pressure and the presence of two types of interfacial interactions, *i.e.*, electrostatic interactions for Fe_2O_3 and dipole-dipole interactions by the PANI fillers with the P(VDF-HFP) copolymer matrix. As mentioned above, in the case of the PANI filler, the presence of the $(=\text{N}-\text{H})^+$ group and the $-\text{CF}_2$ group of P(VDF-HFP) stimulate the interfacial dipole-dipole interaction, which favors the highly polar trans-conformation for the higher yield of piezoelectric β -phase formation (Thakur et al., 2015; Khalifa and Anandhan, 2019; Saïdi et al., 2013). This type of interaction can affect the

TABLE 2 Performance comparison of P(VDF-HFP)-based PEGs of 'hfp' film and 'hfp-f^e', 'hfp-pⁿ', and 'hfp-f^e-pⁿ' composite films.

PDMS with piezoelectric components	Filler	Film	Output voltage (V)
P(VDF-HFP)	–	hfp	0.3
P(VDF-HFP)	Fe ₂ O ₃	hfp-f ^e	1
P(VDF-HFP)	PANI	hfp-p ⁿ	1.2
P(VDF-HFP)	Fe ₂ O ₃ /PANI	hfp-f ^e -p ⁿ	8

spherulitic and granular morphology of P(VDF-HFP) and PANI, respectively, leading to the emergence of a new morphology, as observed in the FE-SEM images (Saïdi et al., 2013). It was also reported that the experimental introduction of ferrite particles such as Fe₂O₃ could nucleate the electroactive β -phase and exhibit both piezoelectric and magnetic properties for the fabricated composites (Andrew and Clarke, 2008). In the case of Fe₂O₃, negative charges electrostatically interact with the –CH₂ dipoles of P(VDF-HFP) responsible for the nucleation of the β -phase, which is also supported by the shifting of –CH₂– asymmetric (ν_{as}) and symmetric (ν_s) stretching, as shown in Figure 1b (Ongun et al., 2020; Lei et al., 2024; Yempally et al., 2023). In addition, the large accumulation of charge carriers at the interface between Fe₂O₃/PANI particles and P(VDF-HFP) chains leads to an increase in the dielectric nature due to the decrease in filler–filler distances, and that promotes more –CH₂–/–CF₂– dipole–dipole polarization in the 'hfp-f^e-pⁿ' composite (Parangusan et al., 2021). So, under compressive stress producing deformation in the piezoelectric β -phase crystalline –CH₂–/–CF₂– molecular dipoles, there is a potential difference between the electrodes. In response, the potential produced by the dipoles must be balanced, and external free electrons accumulate on both sides of the PEG and gradually flow through the external circuit, generating an electric impulse (+ve peak). When the external pressure on the PEG is removed, electrons gradually flow back in the opposite direction, generating an electric impulse in the inverse direction (–ve peak). The variation in the output voltage through the outer resistor (R_L) of the 'hfp-f^e-pⁿ' film-based PEG has also been evaluated and is shown to gradually increase with increasing resistances and reaches a certain value (i.e., ~1016 mV) saturated at a very high resistance, as shown in Figure 6c. The instantaneous power output is calculated using Equation 6 as follows:

$$W = \frac{V^2}{R_L}, \quad (6)$$

where 'V' is the output voltage across the load resistance and ' R_L ' reaches up to 10.3 nW at a typical value of ~10 M Ω of resistance. In addition to instantaneous output voltage, to demonstrate the application of the PEG as a DC power source, it was connected to the capacitors (e.g., 1, 2.2, and 4.7 μ F) of different capacitances separately through a full-wave bridge circuit for successfully charging up via a repetitive touch and release motion by the finger on the surface of the PEG made with the 'hfp-f^e-pⁿ' film, as shown in Figure 6b. Based on the capacitor charging performance curves, the power stored in the

capacitors was calculated using Equation 7 as follows:

$$P = \frac{CV^2}{2t}, \quad (7)$$

where 'C' is the capacitance of the capacitor, 'V' is the saturation voltage, and 't' is the time the capacitor takes to reach a steady state, as shown in Figure 6d. So, the performance of capacitor charging of the PEG indicates its suitability in effectively harvesting the mechanical energies from finger impact, thus making it a potential alternative in the area of self-powered energy harvesting devices. We are also able to lighten white and red LEDs by the 'hfp-f^e-pⁿ' PEG instantly connected in series through a typical bridge circuit, as shown in ESI† (Supplementary Figure S6) and illustrated in video file 1 (ESI†) by the repetitive finger press and release cycle, where no storage device is used. For a better understanding, we have included some previously reported publications and their results in performance and compare their results, as shown in Tables 2, 3. We have also checked the piezoelectric response performances of different PEGs prepared with 0.2, 0.4, 0.8, and 1 wt% of both Fe₂O₃ and PANI using finger impact and included the performance comparisons, as shown in ESI† (Supplementary Figure S7). It should be noted that piezo-voltage arising in the copolymer P(VDF-HFP) composite films is due to the change in dipole moment in aligned molecular dipoles (i.e., –CH₂–/–CF₂–) existing in the molecular chain conformation. As previously mentioned, Fe₂O₃ and PANI used in the 'hfp-f^e-pⁿ' composite result in the formation of more than 99% electroactive phases (F_{EA}) at a 0.6 wt% concentration, and the decrease in the β -phase content in the composite is due to the formation of the δ -phase (α_p -phase). This δ -phase may contribute to dipole moment in aligned molecular dipoles along with the β - and γ -phases, which shows higher piezo voltage for the 'hfp-f^e-pⁿ' composite containing a lower β -phase (a comparative table was presented in supporting electronic information data file, Supplementary Table S1) (Mishra et al., 2022; Gupta et al., 2021). We have also checked the cycling stability and durability of "hfp-f^e-pⁿ" (PEG). For the cycling test, the output performance of the PEG was monitored for at least up to 500 cycles, and the durability test was performed at monthly intervals of 4 months under applied forces using finger impact, and the corresponding results are shown in Figures 7a, b. Interestingly, the piezoelectric output voltage of the PDMS-encapsulated 'hfp-f^e-pⁿ' PEG was more or less repeatable and had a loss of ~2% in the second month, ~4% in the third month, and ~8% in the fourth month.

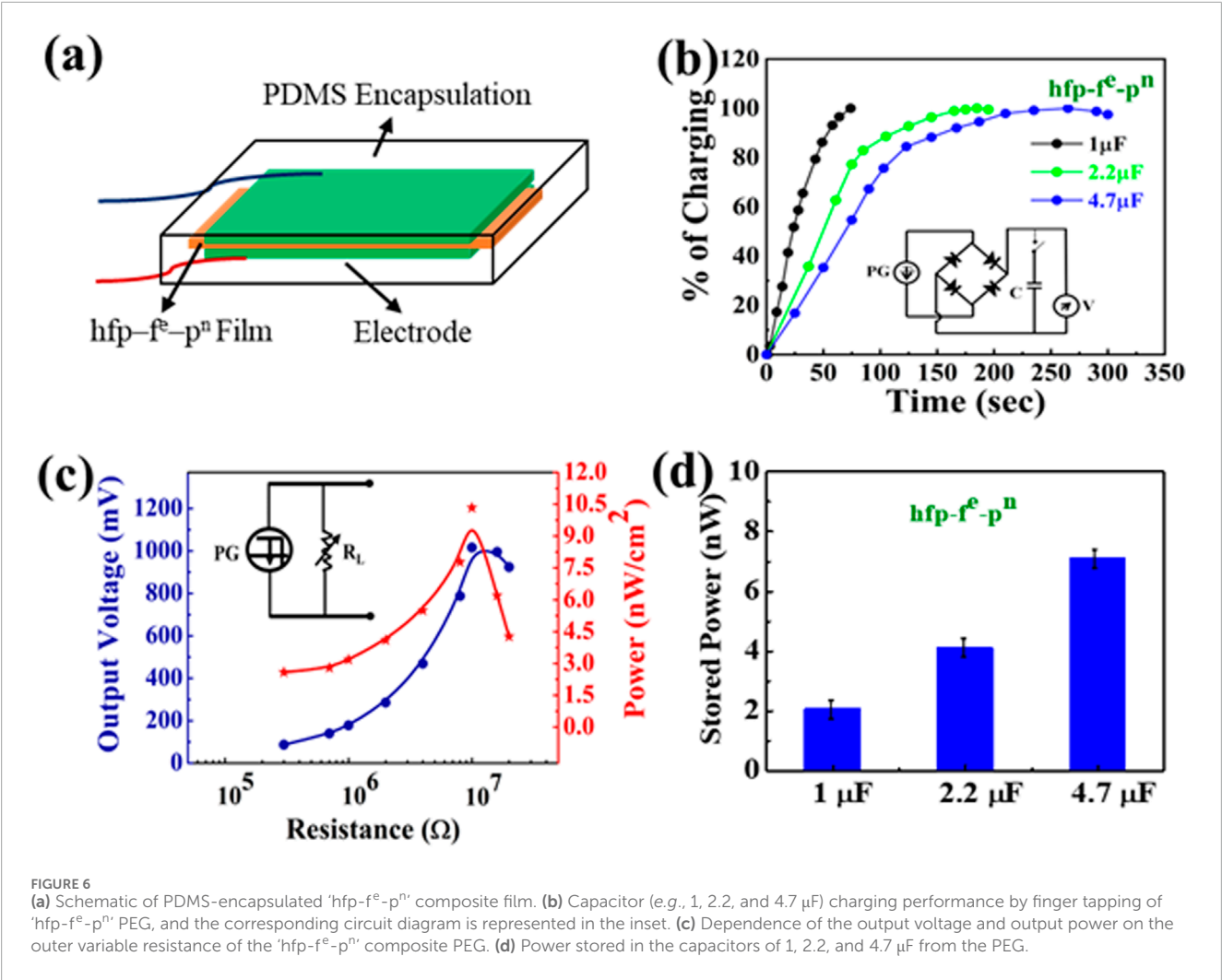


TABLE 3 Performance comparison of various PVDF-based PEGs.

PDMS with piezoelectric components	Filler	Output voltage (V)	β (%) and W	Reference
PVDF	MWCNT	6	68.4 and 81.8 nW	Yu et al. (2013)
P(VDF-HFP)	ZnO	2.8	76.03 and 47 nW	Tohluébaji et al. (2021)
PVDF	PZT	0.18	70 and 30.69 μW/cm ²	Chamankar et al. (2020)
P(VDF-HFP)	Carbon black (CB)	4	80 and 5 μW	Wu et al. (2014a)
P(VDF-HFP)	AgNWs	2.14	89 and 10.16 W/m ³	Wu et al. (2014b)
P(VDF-HFP)	PANI/ZnS microspheres	3	55 and 2.92 μW/cm ²	Parangusan et al. (2021)
PVDF	CoFe ₂ O ₄ NPs	0.018	86 and 11.83 μW	Koc et al. (2022)
P(VDF-HFP) nanofibers	Cellulose nanocrystals	3.8	88.1 and 0.003 μW/cm ²	Jiawei Chen et al. (2024)
PVDF nanofibers	LiCl	5	94 and 0.3 μW/cm ²	Mokhtari et al. (2020)
P(VDF-HFP)	Fe ₂ O ₃ /PANI (hfp-f ^e -p ⁿ Film)	8	75 and 10.3 nW	Present Work

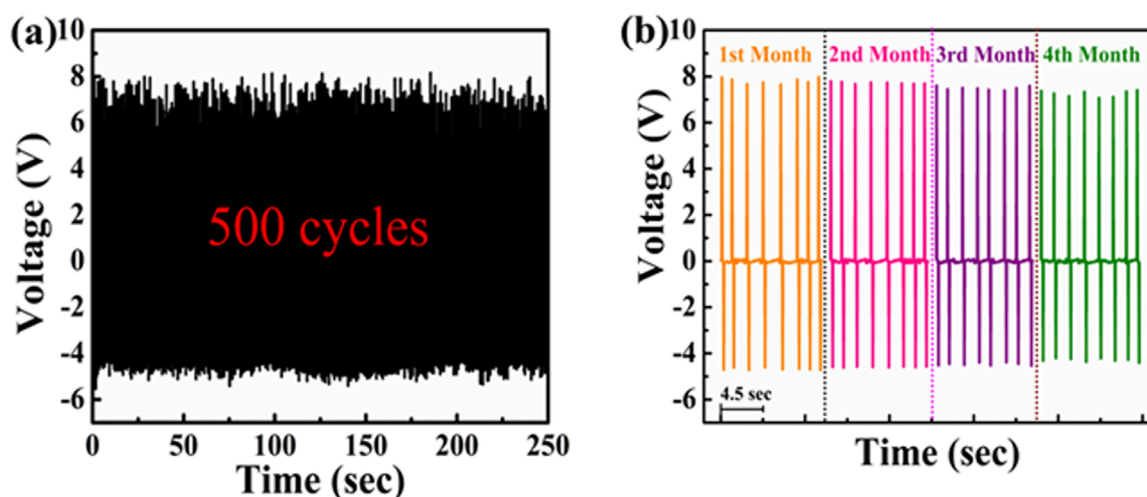


FIGURE 7
(a) Cycling stability test up to 500 cycles and (b) durability test for 4 months of the PDMS-encapsulated 'hfp-f^e-pⁿ' PEG.

4 Conclusions

This work emphasized inducing a large proportion (~99%) of the electroactive β - and γ -phases in copolymer P(VDF-HFP) using fillers (*i.e.*, Fe₂O₃ and PANI), and the films have been prepared by a simple solution-casting method without any mechanical, electrical, or thermal treatment. It is observed that electroactive phases can be enhanced, which is essential for fabricating the piezoelectric-based generator, by optimizing the incorporated external additives, as revealed by ATR and XRD investigations. The surface morphological study showed distinct differences between the 'hfp' film and the 'hfp-f^e-pⁿ' composite film, and it can be signified as a different phase formation in the composites. The PEG composed of 'hfp-f^e-pⁿ' composite film can generate an open-circuit voltage of ~8 V and an output power of 10.3 nW just by finger tapping. The charging capability of the capacitors (*e.g.*, 1, 2.2, and 4.7 μ F) of the composite film within a very short time reflects its potential applicability for piezoelectric-based energy harvesting applications in self-powered technologies to utilize the environmental vibrations available around us. Thus, it is very promising for several possible implementations, such as wearable technology, biomedical sensing, health monitoring, environmental protection, and even security.

Data availability statement

The original contributions presented in the study are included in the article/[Supplementary Material](#) further inquiries can be directed to the corresponding authors.

Author contributions

PB: conceptualization, data curation, formal analysis, methodology, resources, software, visualization, writing –

original draft, and writing – review and editing. AB: formal analysis, validation, resources, writing – review and editing. SA: formal analysis, resources, validation, and writing – review and editing. DR: formal analysis, resources, and writing – review and editing. MR: investigation, methodology, and writing – review and editing. SG: data curation, software, supervision, validation, and writing – review and editing. PA: funding acquisition, investigation, supervision, and writing – review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenrg.2025.1570397/full#supplementary-material>

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