Research Article

Dan Lei, Ning Hu, Liangke Wu*, Rongyi Huang, Alamusi Lee, Zhaonan Jin, and Yang Wang

Preparation of efficient piezoelectric PVDF–HFP/Ni composite films by high electric field poling

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Abstract: Poly(vinylidene fluoride) (PVDF) and its copolymers have been widely studied due to their excellent piezoelectricity and ferroelectricity. In this study, composite films are prepared by adding Ni nanoparticles (0.00–0.3 wt%) into poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP) matrix by solution casting, uniaxial stretching, and high electric field poling. It is found that when the maximum electric field $E_{\max}$ for poling is 130 MV m^{-1} , the calibrated open circuit voltage of the pure PVDF–HFP films reaches 3.12 V, which is much higher than those poled by a lower electric field (70 MV m^{-1} : 1.40 V; 90 MV m^{-1} : 2.29 V). This result shows that the effect of poling on the generated output voltage is decisive. By adding 0.1 wt% Ni nanoparticles, it increases to 3.84 V, 23% higher than that of the pure PVDF–HFP films. To further understand the enhancement mechanism, the effects of Ni nanoparticles on initial crystallization, uniaxial stretching, and high electric field poling are investigated by X-ray diffraction, scanning electron microscope, Fourier transform infrared spectroscopy, and differential scanning calorimetry.

Keywords: piezoelectricity, Ni nanoparticles, PVDF–HFP composite, poling

1 Introduction

Compared to the commonly used lead zirconate titanate, poly(vinylidene fluoride) (PVDF) and its copolymers have a number of advantages, such as light weight and good piezoelectricity, and are more flexible than inorganic piezoelectric materials [1–3]. The high flexibility makes them more suitable for application scenarios requiring large bending and twisting [4]. However, the piezoelectric conversion capability of PVDF is relatively lower, so the improvement of piezoelectricity is desired.

PVDF is a semicrystalline polymer possessing three conformations (TTTT, TGTG', and T₃GT₃G') and at least five crystal phases (α , β , δ , γ , and ϵ). Among the phases, the α -phase is the most common and stable one exhibiting a monoclinic structure, and it is a nonpolar crystal with the gauche-trans-gauche' (TGTG') conformation with no piezoelectricity. The β -phase exhibits the orthorhombic structure with the all-trans (TTTT) conformation with the best piezoelectricity. Hence, increasing the β -phase content is extremely important in the preparation of high piezoelectric materials [5–12]. As a result, the transformation from the α -phase to the β -phase is a leading research topic in recent years. A number of methods, such as uniaxial stretching [13–19], high electric field [20], annealing [21,22], high-pressure [23], and adding nanoparticles, have been widely used to prepare PVDF films with a high fraction of β -phase.

Nanofiller addition has been investigated in many studies. Kim *et al.* studied the effect of multiwalled carbon nanotubes (MWCNT) on the crystal structure of PVDF films. It is found that for stretched films, the addition of MWCNT can increase the fraction of β -phase by increasing the crystallization rate of the films [20]. Wu *et al.* added carbon black (CB) to poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP) to prepare PVDF–HFP/CB composite films by the solution casting method. When the CB content is 0.5 wt%, the open circuit voltage and density of the harvested power reach the highest values, which are 104%, 364% (AC circuit), and 461% (DC circuit) higher than those of pure PVDF–HFP films, respectively [24].

* **Corresponding author: Liangke Wu**, College of Aerospace Engineering, Chongqing University, Chongqing 400044, China, e-mail: wuliangke@cqu.edu.cn, tel: +86-02365102510

Dan Lei, Rongyi Huang, Zhaonan Jin, Yang Wang: College of Aerospace Engineering, Chongqing University, Chongqing 400044, China

Ning Hu: College of Aerospace Engineering, Chongqing University, Chongqing 400044, China; State Key Laboratory of Reliability and Intelligence Electrical Equipment, School of Mechanical Engineering, Hebei University of Technology, Tianjin 300401, China

Alamusi Lee: State Key Laboratory of Reliability and Intelligence Electrical Equipment, School of Mechanical Engineering, Hebei University of Technology, Tianjin 300401, China

Bhattacharjee *et al.* added surface-functionalized spherical magnetite nanoparticles Fe_3O_4 of different sizes into PVDF to prepare composite piezoelectric films by solution casting, and the increase in the relative fraction of polar β -phase is verified by X-ray diffraction (XRD) and Raman spectroscopy [25]. Ponnammam *et al.* blended NiFe_2O_4 nanoparticles to poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP) by electrospinning to prepare composite nanofibers. When the content of NiFe_2O_4 is 2 wt%, the output voltage reaches 4 V, exhibiting high potential in the design of piezoelectric devices [26].

At present, the study has been focused on the dielectric properties, magnetoelectric coupling, and electromagnetic shielding of Ni nanoparticles to PVDF. Only a few reports have been conducted to study the effects of low-content Ni nanoparticles on enhancing the piezoelectric properties of PVDF. Li *et al.* compressed Ni nanoparticles and PVDF powder into flake samples to prepare composite materials with high dielectric constant and low loss permeability. The results show that Ni and PVDF can produce compression-induced percolation. At 100 Hz, the maximum dielectric permittivity is ten times that of the noncompressed samples, and the low-frequency dielectric loss can be controlled within the range of 0–0.15 [27]. They also studied the stretching effects on the PVDF/Ni films and confirmed the threshold elongation ratio in the composites. At 100 Hz, the conductivity is increased by 4–5 orders of magnitude. When the elongation ratio reaches the threshold, the maximum dielectric permittivity is 17 times that of the unstretched samples [28].

In this study, PVDF–HFP powder was added into the suspension of Ni nanoparticles mixed with *N,N*-dimethylformamide (DMF) to prepare PVDF–HFP/Ni composite films by the solution casting method. By adjusting the content of Ni nanoparticles in the composite films, the high piezoelectric films were prepared. The effects of Ni nanoparticles on the piezoelectricity of the composite films during the initial crystallization, stretching, and

poling processes were studied by XRD, Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and differential scanning calorimetry (DSC) techniques.

2 Experimental

2.1 Material

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP) (Kynar Flex 2801) was purchased from Arkema Inc., USA, DMF was supplied by Shanghai Titan Scientific Co. Ltd., Shanghai, China, and Ni nanoparticles were provided by Zhong Ye Xin Dun Alloy Co. Ltd., Hebei province, China. The SEM images of Ni nanoparticles are shown in Figure 1. The properties of PVDF–HFP, DMF, and Ni nanoparticles are presented in Table 1. All materials were used as received.

2.2 Piezoelectric film preparation

The preparation process of PVDF–HFP/Ni composite films is similar to the method of our earlier reports [24,29,30], which includes three main stages, that is, initial crystallization, stretching, and poling. In this study, the Ni contents are 0, 0.05, 0.075, 0.1, 0.2, and 0.3 wt%, respectively. The process is shown in Figure 2 and can be described as follows:

- (1) Initial crystallization: (a) Add a moderate mass of Ni nanoparticles (depending on the Ni contents) into 24 g DMF solvent and mix them by using an ultrasonic machine. (b) Add 8 g PVDF–HFP powder into the mixture solution. (c) Stir the mixture by using the ultrasonic machine and a planetary mixer and finish it by a defoaming process. (d) Pour the homogeneous

Figure 1: SEM images of Ni particles: (a) magnification: 20k and (b) magnification: 50k.

Table 1: Properties of PVDF–HFP, DMF, and Ni nanoparticles

PVDF–HFP	Melting temperature	140~145 °C	Water absorption (23 °C, 24 h)	0.03%
	Density	1.76~1.80 g cm ⁻³	Melt viscosity (232 °C, 100 s ⁻¹)	2300~2700 Pa s
	Refraction index	1.41	Melt flow rate (232 °C, 125 kg)	0.35~0.75 g min ⁻¹
DMF	Density	0.945 g cm ⁻³	Melting temperature	–61 °C
	Boiling temperature	153 °C	Flash point	58 °C
	Purity (%)	≥99.5% (GC)		
Ni nanoparticles	Appearance	Sphere	Diameter (nm)	100~300
	Purity (%)	99.95%		

mixture onto three Al plates (10 cm × 7.5 cm × 0.1 cm). (e) Place the Al plates on the heating plates at 90 °C for 1–2 h to evaporate the DMF solvent completely. After the initial crystallization, the unstretched PVDF–HFP/Ni films are obtained.

- (2) Stretching: (a) Cut the initial crystallized film into samples of 5 cm × 4 cm (direction to be stretched).

(b) Stretch the films by a tensile testing machine in a temperature-controlled box at about 60 °C. The stretching rate is 10 mm min⁻¹, and the elongation ratio is 4.5–5.5. The thicknesses of the prepared PVDF–HFP/Ni films are shown in Table 2, and the stretched PVDF–HFP/Ni films are shown in Figure 3. It is observed that with the increment of Ni contents, the films become darker.

Figure 2: Preparation process of PVDF–HFP/Ni composite films.

Table 2: The thicknesses of the prepared PVDF–HFP/Ni composite films (μm)

Ni content (wt%)	0	0.05	0.075	0.1	0.2	0.3
1	72	71	72	78	70	66
2	71	79	69	76	64	66
3	70	80	70	66	63	81
Average	71	77	70	73	66	71

- (3) Poling: (a) Use conductive epoxy (CW 2400) to bond $15\ \mu\text{m}$ thick Al electrodes on both sides of the stretched film (size: $2.5\ \text{cm} \times 3\ \text{cm}$ [stretching direction]) to prepare a piezoelectric element. (b) Keep the films at room temperature for 24 h for complete curing of the conductive epoxy. (c) Apply the step-wise poling method on the films. The initial electric field is $20\ \text{MV m}^{-1}$, the increment for each step is $10\ \text{MV m}^{-1}$, and the maximum electric field E_{max} is $130\ \text{MV m}^{-1}$. For each step, the poling interval is 8 min, and the pause time is 4 min. As the poling temperature can significantly affect the piezoelectricity, the poling temperature remains at $25\ ^\circ\text{C}$ for all samples [31]. The poling electric field is illustrated in Figure S1.

2.3 Electrical experiments

Three films with the same content of nanoparticles are attached on an Al plate ($200\ \text{mm} \times 100\ \text{mm} \times 1\ \text{mm}$), and then conductive wires are connected on both sides for the open circuit voltage tests. The experimental setup is shown in Figure 4. The Al plate is fixed on a mass. A sinusoidal AC signal ($f = 25\ \text{Hz}$, the resonance frequency of the system) is generated by a function generator and passes through an amplifier applied on the electromagnet coil. Then, the induced magnetic field forces the magnet at the end of the Al plate to vibrate periodically, leading

to the periodical deformation of piezoelectric films and the generation of periodical voltages. The output voltages are recorded by an oscilloscope. To accurately calculate the calibrated open circuit voltage, the displacement of the Al plate end measured by the laser displacement sensor is maintained at approximately 1 mm. In this study, the piezoelectric films work in the 31 mode, as shown in Figure S2.

2.4 Characterization of PVDF–HFP/Ni composite films

In this study, XRD, FTIR, DSC, and scanning electron microscope (SEM) are used to analyze the crystal evolution during the preparation process. For simplicity, U, S, and P represent “unstretched,” “stretched,” and “stretched plus poled” samples, respectively. For example, 0.075U refers to the unstretched film containing 0.075 wt% Ni particles. In XRD spectra, the angle 2θ ranges from 15° to 30° , the step is 0.02° , and the scanning rate is $1^\circ\ \text{min}^{-1}$. In FTIR spectra, the wavenumber ranges from $4,000$ to $400\ \text{cm}^{-1}$, but the interval ($1,000$ – $600\ \text{cm}^{-1}$) is shown in the study. In DSC, the films are kept at $40\ ^\circ\text{C}$ for 5 min, and then heated to $200\ ^\circ\text{C}$ by $10\ ^\circ\text{C min}^{-1}$. For SEM observation, the films are kept in liquid nitrogen, and then fractured to obtain a uniform fracture, which is sprayed gold on the surface for 25 s.

3 Results and discussion

3.1 Open circuit voltage

Earlier studies have shown that the open circuit voltage V is proportional to the film thickness t and the plate end

Figure 3: Stretched films with different contents of Ni particles (wt%). The arrow shows the stretching direction. (a) Stretched films and (b) stretched films for piezoelectric elements preparation.

Figure 4: Electrical experimental setup.

displacement Δl of the film. Under the small deformation, Δl is proportional to the plate tip displacement u , and V is proportional to u [29]. To compare the piezoelectric properties of different piezoelectric films, the calibrated open circuit voltage V_c is calculated as follows:

$$V_c = V \frac{u_0 t_0}{ut}, \quad (1)$$

where V is the recorded voltage, u is the plate tip displacement, t is the thickness of the film, $u_0 = 1 \text{ mm}$ is the standard displacement, and $t_0 = 100 \mu\text{m}$ is the standard thickness.

Figure 5 shows the calibrated open circuit voltages of the PVDF–HFP/Ni piezoelectric composite films. It is found that when the maximum electric field $E_{\text{max}} = 70 \text{ MV m}^{-1}$, the calibrated open circuit voltage of the pure PVDF–HFP films is 1.41 V [30], and it increases to 2.29 V when $E_{\text{max}} = 90 \text{ MV m}^{-1}$ [32]. In this study, when the maximum electric field E_{max} reaches 130 MV m^{-1} , it increases to 3.12 V, which is 123 and 36% higher than those samples poled by 70 and 90 MV m^{-1} . The results confirm the decisive effect of poling on the piezoelectricity. As the electric breakdown occurs when E_{max} is more than 130 MV m^{-1} , the maximum electric field is set as 130 MV m^{-1} . It is found that the calibrated open circuit voltage increases with the content of Ni until 0.1 wt% (3.84 V) and then decreases gradually. When the content of Ni nanoparticles reaches 0.3 wt%, the nanoparticles are obviously agglomerated and unevenly dispersed, which hinders the phase transformation from α -phase to β -phase,

resulting in a lower piezoelectric performance. The results show a significant improvement effect of Ni on the piezoelectricity of PVDF–HFP. It is also found that the extremely high electric field can enhance the generated voltage dramatically, which may be more important than the addition of nanofillers. It has been reported that the saturation poling voltage is about 150 MV m^{-1} [33]. In this study, E_{max} is close to 150 MV m^{-1} , indicating that the effect of nanofiller addition is not so significant compared with the samples poled at lower electric fields [32].

Figure 5: The calibrated open circuit output voltage of PVDF–HFP/Ni films.

Figure 6: SEM cross-sectional images of PVDF–HFP/Ni composite films (initial crystallized): (a) 0.05 wt% ($\times 20k$), (b) 0.1 wt% ($\times 20k$), and (c) 0.3 wt% ($\times 20k$).

3.2 Structure and morphology of PVDF–HFP/Ni composite films

Figure 6 shows the SEM cross-sectional images of the initial crystallized composite films. Figure 6(a) shows the film containing 0.05 wt% Ni nanoparticles. It is observed that there is no agglomeration of nanoparticles, and the dispersion is relatively uniform. Figure 6(b) shows the film containing 0.1 wt% Ni nanoparticles. The crystal defects may be caused by the

addition of the fillers. It can be seen that the distribution of nanoparticles is relatively uniform, and the agglomeration is not obvious. From Figure 6(c), it is found that the nanoparticles are significantly agglomerated, unevenly dispersed, and closely connected to the matrix. The results indicate that the agglomeration of the nanoparticles becomes more obvious, and the dispersion becomes more uneven with the increase of the Ni content. The proper content of Ni is determined as 0.1 wt%, which does not lead to obvious agglomeration.

Figure 7: XRD spectra of PVDF–HFP/Ni composite films: (a) unstretched films, (b) stretched films, and (c) stretched plus poled films.

3.3 Phase transformation of PVDF–HFP/Ni composite films

3.3.1 XRD

Figure 7 shows the XRD spectra of PVDF–HFP/Ni composite films at three stages, i.e., initial crystallized, stretched, and poled. In Figure 7(a), the characteristic peaks appear at 18.4° , 20.0° , and 26.6° , corresponding to the (100), (110), and (021) planes of the α -phase, respectively. At this time, the β -phase is not so obvious. It shows that after the initial crystallization, the α -phase dominates. In Figure 7(b) and (c), the peak appears at 20.4° , corresponding to the (110) plane of the β -phase [9,34–36]. In the stretched films, the α -phase almost completely disappears, indicating that a complete phase transformation from α -phase to β -phase occurs during the stretching process. Compared to stretched films, the stretched plus poled films show no obvious differences because the α -phase content is close to zero, and thus a little phase transformation occurs during the poling stretching.

3.3.2 FTIR

Figure 8(a)–(c) shows the FTIR spectra of PVDF–HFP/Ni composite films. The wavenumber interval is $1,000\text{--}600\text{ cm}^{-1}$. The peaks at 489, 614, 765, 795, 855, and 976 cm^{-1} correspond to the α -phase, whereas the peaks at 510, 840, and $1,279\text{ cm}^{-1}$ correspond to the β -phase [9,10,14,37]. In Figure 8(a), the peaks corresponding to the α -phase are obvious in the films of the 0U, 0.05U, and 0.075U. With the increase of Ni nanoparticle content, the peaks corresponding to the α -phase become weaker. Meanwhile, the peaks corresponding to the β -phase increase, indicating that the addition of Ni nanoparticles can induce the formation of the β -phase during the initial crystallization stage. In Figure 8(b)–(c), the peaks of the α -phase almost disappear and the peaks of the β -phase become much more obvious after stretching and poling. It is consistent with the XRD results, which proves that the α -phase is transformed into the β -phase in the stretching stage and poling has little effect on phase transformation.

The relative fraction of the β -phase $F(\beta)$ can be calculated by the following equation [7]:

Figure 8: FTIR spectra of PVDF–HFP/Ni composite films: (a) unstretched films, (b) stretched films, (c) stretched plus poled films, and (d) relative fraction of β -phase in PVDF–HFP/Ni composite films.

Table 3: Relative fraction of β -phase in PVDF-HFP/Ni composite films

Ni content (wt%)	0.00	0.05	0.075	0.1	0.2	0.3
U(%)	34	36	38	96	95	96
S(%)	92	94	97	97	95	97
P(%)	96	98	98	98	98	94

$$F(\beta) = \frac{A_{\beta}}{\left(\frac{K_{\beta}}{K_{\alpha}}\right)A_{\alpha} + A_{\beta}} = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}}, \quad (2)$$

where, K_{α} is $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, K_{β} is $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, and A_{α} and A_{β} are the absorbencies at 766 cm^{-1} , respectively. The calculation method of the relative fraction of the β -phase is instructed in Figure S3. Table 3 and Figure 8(d) show the calculated results.

From Figure 8(d) and Table 3, it is concluded that the relative fraction of the β -phase is very low when the Ni nanoparticle content is low ($<0.1 \text{ wt}\%$) in the initial crystallization stage. However, in the films containing high

contents of Ni nanoparticles, $F(\beta)$ is more than 95%, even without stretching and poling, indicating that the Ni nanoparticles have an obvious effect on the α -phase to β -phase transformation. From the result, it can be concluded that the threshold value for Ni nanofillers in PVDF-HFP matrix may be about $0.1 \text{ wt}\%$; therefore, a sudden increase of $F(\beta)$ occurs when the Ni content is more than $0.1 \text{ wt}\%$. The effects of stretching on the α -phase to β -phase transformation are obvious. From our earlier study, when the elongation ratio is more than 3, the relative fraction of β -phase $F(\beta)$ increases dramatically. Based on the results of the open circuit voltages, the optimal elongation ratio is 5. As a result, in this study, the elongation ratio is set as 5 [31]. All stretched samples exhibit an $F(\beta)$ value of more than 90% because the induced stress on the molecular chains leads to the elongation of molecular chains, which is preferred to form fibrillar-like molecular chains (corresponding to β -phase). However, for the films containing high contents of Ni nanoparticles, $F(\beta)$ shows minimal changes after stretching because $F(\beta)$ is quite high in the initial crystallization stage. The other function of stretching is to force the

Figure 9: DSC thermograms of PVDF-HFP/Ni composite films: (a) unstretched films, (b) stretched films, (c) stretched plus polarized films, and (d) crystallinity degree of PVDF-HFP/Ni composite films.

molecular chains to align along the stretching direction. Hence, stretching is also necessary for the high $F(\beta)$ films to obtain piezoelectricity. For all poled films, $F(\beta)$ remains nearly the same, indicating the crystal phase transformation has been completed during stretching. The main effect of poling is to force the dipole moments of the β -phase molecular chains to align along the direction of the electric field, and thus the piezoelectricity can be obtained. For low $F(\beta)$ films, the phase transition can also be promoted by the high electric field.

3.4 Crystallization of PVDF–HFP/Ni composite films

Figure 9 shows the DSC thermograms of the PVDF–HFP/Ni films. In this study, we use the following equation to calculate the crystallinity degree of PVDF–HFP composite films at different stages [38]:

$$X_c = \left(\frac{\Delta H_m}{\Delta H_m^\phi} \right) \times 100\%, \quad (3)$$

where ΔH_m is the melting enthalpy of the material calculated by the DSC supporting software, and ΔH_m^ϕ is the melting enthalpy of the 100% crystalline PVDF–HFP material, that is, 104.5 J g^{-1} . The results are shown in Figure 9(d).

From Figure 9(d), the crystallinity degree of all films at the initial crystallization stage is nearly the same (31–33%). However, the crystallinity degree of the stretched films is generally higher than those at the initial crystallization stage, which has been reported earlier [13]. The crystallinity degree of 0.3U reaches the maximum value of 39%, indicating the induced stress during the stretching process leads to the reorganization of molecular chains in the amorphous area. Besides, for the poled films, the crystallinity degree of 0.075SP, 0.1SP, and 0.2SP samples is lower than those of the nonpoled films. A similar result has been reported in PVDF/CNT composites [39], and it may be related to the negative effect of Ni nanoparticles during the reorganization of molecular chains. Another reason may be attributed to the partial destruction of the crystalline structure caused by the poling process [40–42]. Comparing Figure 9(a) and (b) with Figure 9(c), the melting point of poled films is lower than nonpoled films, and it may be explained as follows: the crystalline structure of the poled films presents less entropy, compared with that of the nonpoled films. As is well known, the application of poling can force the dipolar moments to align along the direction of the electric field, which can lead to a more oriented structure, resulting in the lower melting temperature [41–43].

4 Conclusions

In this study, high piezoelectric composite films are prepared by an extremely high poling electric field and Ni nanoparticles addition. The maximum electric field $E_{\max}$ is as high as 130 MV m^{-1} and the calibrated open circuit voltage of the pure PVDF–HFP films reaches 3.12 V, which is much higher than those poled by a lower electric field. The piezoelectricity can be further enhanced by adding Ni nanoparticles. When 0.1 wt% Ni nanoparticles are added, the calibrated open circuit voltage reaches the maximum value (3.84 V), which is about 123% of the pure PVDF–HFP film prepared by the same process. The experimental method of extremely high electric field poling and Ni nanoparticles addition reported in this study is facile and of low cost for preparing efficient piezoelectric films. Besides, the crystallinity evolution in the preparation process is investigated by SEM, XRD, FTIR, and DSC.

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