Research Article

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Influences of poling temperature and elongation ratio on PVDF-HFP piezoelectric films

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Abstract: Poly(vinylidene fluoride) (PVDF) and its copolymers exhibit excellent piezoelectric properties and are potential materials for high efficiency energy harvesting devices. In this study, poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) films are prepared by the solution casting method. The prepared film is then subjected to mechanical stretching and poling process. By adjusting the temperature of the poling process and the elongation ratio of the mechanical stretching process, the relative content of β-phase $F(\beta)$ increases significantly, leading to high piezoelectric performance. The maximum output voltage of the PVDF-HFP films poled at 40°C reaches 3.67 V, 71% higher than that of the films poled at room temperature. Fourier transform infrared spectroscopy analysis (FTIR), XRD (X-ray diffraction), and differential scanning calorimetry are used to investigate the influences of mechanical stretching and poling process on the crystal structure to discover the enhancement mechanism. This work provides a straightforward and low-cost route to prepare high piezoelectric PVDF-HFP-based materials.

Keywords: PVDF-HFP, stretching, poling, piezoelectricity

1 Introduction

Energy harvesting is a technology that collects distributed energy around the environment and converts it into usable electricity [1]. Current energy collection devices include solar energy collection devices, wind energy collection devices, vibration energy collection devices, *etc.* [2–4]. The power generation mechanisms are mainly static electricity, piezoelectric electricity, and electromagnetic electricity [4], among which the piezoelectric energy harvesting technology has the advantages of fast response, low cost, simple structure, no electromagnetic interference, convenient to handle, and so on ref. [5].

According to the material properties and composition, piezoelectric materials can be classified as single crystals, piezoelectric ceramics, piezoelectric polymers, and piezoelectric composites. Piezoelectric polymers mainly include poly(vinylidene fluoride) (PVDF) and its copolymers, polyvinylchloride and polypropylene [6], which possess the advantages of high chemical corrosion resistance, low mechanical impedance, and excellent flexibility [7], showing extraordinary promise for applications in energy harvesting [8]. PVDF and its copolymers possess the advantages of high piezoelectric coefficient, favorable biocompatibility, wide frequency response, promising flexibility, and easy processing. PVDF assesses at least five crystal phases, *i.e.*, α, β, δ, γ, and ε. The α-phase is monoclinic and the chain configuration is TGTG'. The β-phase belongs to the orthomorphic system and the molecular chain configuration is TTT. The γ-phase is monoclinic and its chain structure is similar to that of the α-crystal phase [7]. Among the phases, the α-crystal phase is nonpolar, so it does not exhibit piezoelectricity. The β-crystal phase is the most strongly polar with excellent piezoelectricity [9]. In most cases, the α-phase dominates in the crystal parts of PVDF. Therefore, increasing the β-phase content plays an extremely important role in the improvement of PVDF's piezoelectricity. At present, uniaxial stretching [10–12], high electric field poling [13–15], high pressure crystallization [16,17], and nanofillers additions [12,18,19] are commonly applied to increase the content of the β-crystal phase.

The influences of poling temperature on piezoelectric properties of materials have been studied in a multitude of reports [21–24]. The poling effects on the piezoelectric properties of 0–3 connectivity PZT Portland cement (PC) composites, including piezoelectric coefficient (d_{33}) and electromechanical coupling factor (k_T), have been

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investigated by Jaitanong and Chaipanich. The results demonstrate that when the poling temperature is set at 130°C, the d_{33} and k_T reach the maximum values [20]. Some researchers also proposed that the piezoelectric ceramics with polycrystalline phase boundary are affected by poling temperature, and the piezoelectric constants are highly sensitive to the poling temperature [21–24].

As mentioned above, most of the published studies about the effects of poling temperature on the piezoelectric properties are focused on piezoelectric ceramics, with only a few on PVDF or other polymers. It was reported that under the poling electric field of 150 MV m^{-1} at 95°C, the nonpolar α-crystal phase can be transformed to the polar β-crystal phase [25]. Darestani *et al*. investigated the piezoelectric properties of piezoelectric PVDF films for separation processes. The specimen was heated from room temperature to 90 ± 10°C, while the poling electric field increased gradually from zero to 2 kV at a rate of ~50 V min^{-1}. The results show that the poling process dramatically changes the microstructure of the films [26]. Most studies emphasized that the structural evolution may be due to the internal rotation of the molecular chains induced by the electric field. It is in consistent with the β-phase formation and the rearrangement of the inherent dipoles in the matrix. In these studies, the effect of the poling on the structure of PVDF is mentioned only when the heating is also carried out during poling [25–27]. Besides, Jan proposed that the relative content of the β-crystal phase increases significantly when the poling temperature is set at 150°C [28]. As a conclusion, both the temperature and the poling electric field may have effects on the piezoelectric properties of the materials by affecting phase evolution and realignment of dipole moments. The content and orientation polarizability of the β-crystal phase are improved when poled at a proper temperature as shown in the experiments. After the optimal poling temperature was obtained, we also varied the elongation ratio during the stretching process to define the optimal preparation parameters.

2 Experiments

2.1 Materials

PVDF can form a number of different copolymers. Poly (vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) is a PVDF copolymer of low crystallinity, but high F content compared with PVDF; consequently, it exhibits better hydrophobicity than PVDF. Besides, PVDF-HFP also exhibits better flexibility and solidification. In terms of piezoelectric properties, when the mixing ratio of HFP is 5%, the piezoelectric coefficient d_{31} of PVDF-HFP can reach 30 p CN^{-1}, which is higher than that of PVDF [29].

Table 1: The properties of PVDF-HFP

Morphology	White powder	Density	1.76–1.8 g cm^{-3}
Melting point	140–145°C	Water absorption	0.03%
Refractive index	1.41	Melt viscosity (232°C, 100 s^{-1})	2,300–2,700 Pa s

The PVDF-HFP powder (Kynar Flex 2801) is produced by Arkema Inc. Its properties are shown in Table 1. The solvent is *N*,*N*-dimethylformamide (DMF) which can be commercially obtained from Shanghai Titan Scientific Co., Ltd.

2.2 Preparation of piezoelectric films

In this study, the solution casting method is used to prepare the initial crystallized films. The preparation process of the initial crystallization films mainly includes the following steps as shown in Figure 1: (1) add moderate PVDF-HFP powder into DMF solution (mass ratio: PVDF-HFP:DMF = 1:3) by a planetary machine for 5 min and an ultrasonic machine for 5 min, then by a planetary machine for 5 and 2 min (for defoaming). (2) Pour the DMF/PVDF-HFP mixture evenly onto a 2 mm-thick Al mold whose edges are formed by sponge tapes (9 cm × 16.5 cm) which are removed within 10 min after solution casting, and heat it at 90°C for 2 h; (3) Cut the samples for stretching from the middle of the initial crystallization films, the size is 5.5 cm × 4 cm (stretching direction). The thickness of the initial crystallized films ranges from 180 to 240 μm. (4) Press the initial crystallized film by a heavy flat mass for 24 h. (5) Stretch the films at about 60°C in a temperature-control box (±2°C) with a rate of 10 mm min^{-1} and an elongation ratio R of 4.5–5.5 [14]. The film stretching equipment is shown in Figure 1(c), which includes an EZ-LX tensile testing machine (Shimadzu Manufacturing Co. Ltd., Japan), a homemade temperature-control box, a digital heat gun, a digital thermometer, *etc*. The thickness of the stretched films is 50 to 90 μm, as shown in Figure 2. (6) Attach Al electrodes (t = 15 μm) on both sides of the film by CW2400 conductive epoxy adhesive and keep it for 24 h for complete curing. The poling process was

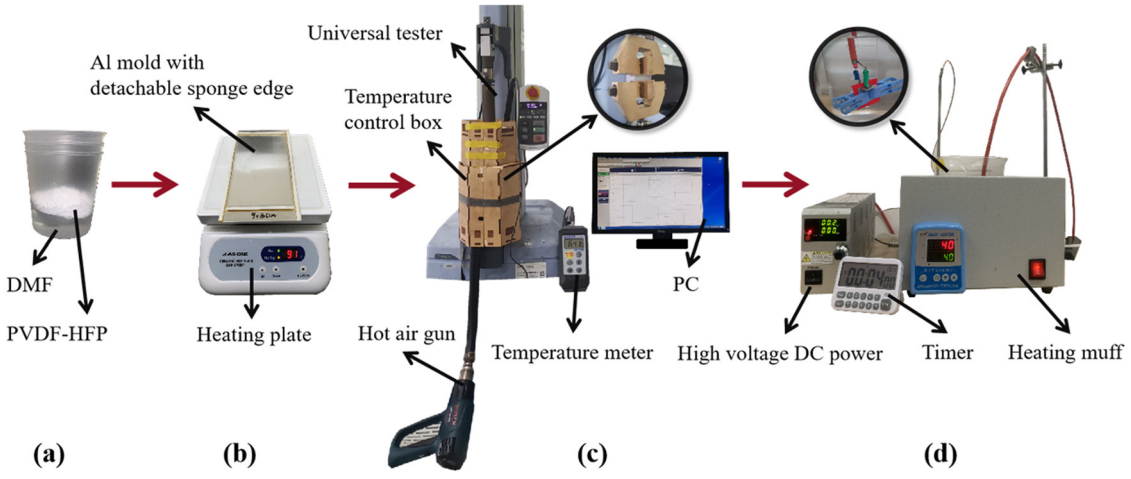

Figure 1: Preparation process of PVDF-HFP piezoelectric films: (a) solution, (b) initial crystallization, (c) uniaxial stretching, and (d) stepwise poling.

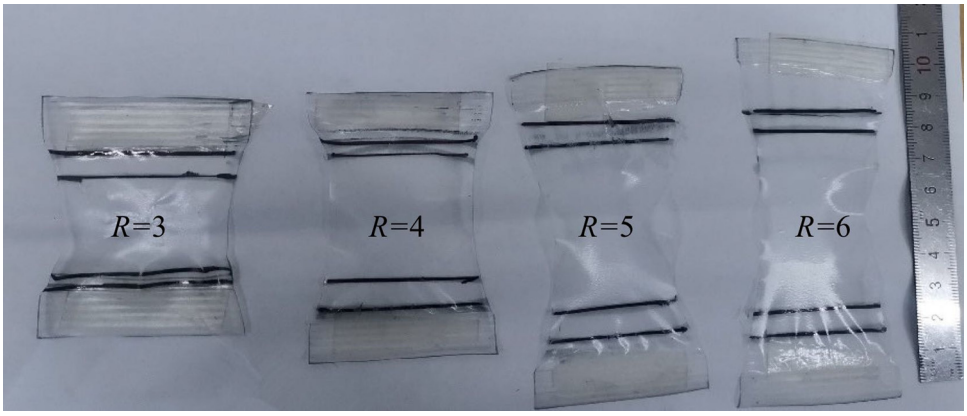

Figure 2: Images of stretched films with different elongation ratios.

carried out in silicone oil at various temperatures by a stepwise method. The voltage source is HJPQ-30P1 (Matsusada Precision Inc.). The initial electric field is 20 MV m^{-1}, and the maximum electric field (denoted as E_{max}) is 90 MV m^{-1}. For each step, the poling time is 8 min, the rest time is 4 min, and the electric field increases by 10 MV m^{-1}.

To study the effects of poling temperature on the piezoelectric properties of PVDF-HFP, the poling temperature (denoted as T_p) is set from 25 to 45°C, and the elongation ratio in the stretching process is kept at 5. Figure 1(d) shows the equipment for poling. The poling is carried out in silicone oil heated by a digital electric heating sleeve (±2°C). After the optimal poling temperature is determined, the elongation ratio varies from 3 to 6 to investigate its effects on piezoelectricity.

The measurement setup of the open circuit voltage is shown in Figure 3. The measurement method is introduced in a previous report [12] and in the Supporting information's Section at the end of the paper.

2.3 Characterization of piezoelectric films

FTIR spectra were used to identify the structure of the polymer backbone, the types and positions of substituents, and the structure of the molecular chains. The equipment used in this study was the Nicolet IS50 Fourier Transform Infrared Spectrometer (Thermo Fisher Scientific Co. Ltd., USA).

X-ray diffraction (XRD) is a technique for structural analysis of crystalline substances. In the characterization

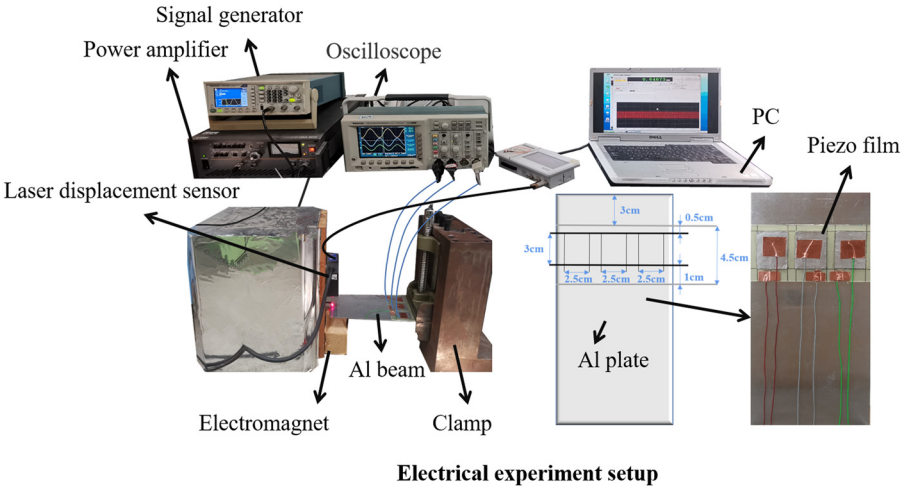

Figure 3: Measurement setup of the open circuit voltage.

of polymers, XRD is mainly used for phase analysis and crystallinity degree determination. In this study, the equipment used for XRD was X 'PERT POWDER X-ray diffractometer (Panaco Co. Ltd., Netherlands).

Differential scanning calorimetry (DSC) is a thermal analysis technique that measures the relationship between temperature and the power difference input into the sample and reference material. It can be used to study the thermal change in the reaction process such as melting, sublimation, and crystallization. The Netzsch DSC 214 Polyma differential scanning calorimeter was used in this study.

3 Results and discussion

3.1 Open circuit voltage

It was proved that the open circuit voltage V is proportional to the film thickness (t) and the displacement (u) of the end of the vibration cantilever [19]. Therefore, the concept of calibrated open circuit voltage (V_c) is introduced in this study to evaluate the piezoelectric properties of different piezoelectric films. The calculation formula of V_c is:

$$V_c = V\frac{u_0 t_0}{ut}, \tag{1}$$

where V is the actual measured voltage, u is the displacement of the end of the aluminum plate, t is the film thickness, u_0 = 1.0 mm is the standard displacement, and t_0 = 100.0 μm is the standard thickness.

Figure 4(a) shows the relationship between the calibrated open circuit voltage and the poling temperature T_p when the elongation ratio is kept at 5. It is shown that the open circuit voltage increases with the poling temperature. However, an excessively high temperature may lead to the electric breakdown at a relatively lower electric field. Figure 4(b) shows the relationship between the calibrated open circuit voltage and the elongation ratio R when the poling temperature is kept at 40°C. From the experimental results, it is observed that the open circuit voltage of PVDF-HFP films increases with poling temperature until 40°C. However, when the poling temperature rises to 45°C, electrical breakdown [30] occurs when the poling electric field intensity is higher than 60 MV m^{-1}. As a result, when the poling temperature is set to 45°C, the maximum electric field of poling is 60 MV m^{-1} (For other samples, E_{max} = 90 MV m^{-1}). When T_p is 40°C and R is 5, the calibrated open circuit voltage reaches the highest value of 3.67 V, which is 71% higher than that of the films poled at room temperature (2.15 V) (Figure 4(a)). When T_p is 45°C and the maximum poling electric field E_{max} is 60 MV m^{-1}, the calibrated open circuit voltage is only 2.05 V. Thus, the optimal poling temperature in this study is determined to be 40°C.

At the optimal poling temperature of 40°C, the open circuit voltages of films stretched by different elongation ratios (3–6) were also measured. The experimental results showed that the open circuit voltage increases with R until 5 (V_c = 3.67 V) and then decreases (Figure 4(b)). It is found that the open circuit voltage increases with the elongation ratio and reaches the maximum value at R = 5 and then decreases. The phase transformation mainly occurs when R < 4, thus $F(\beta)$ remains nearly unchanged when R > 4.

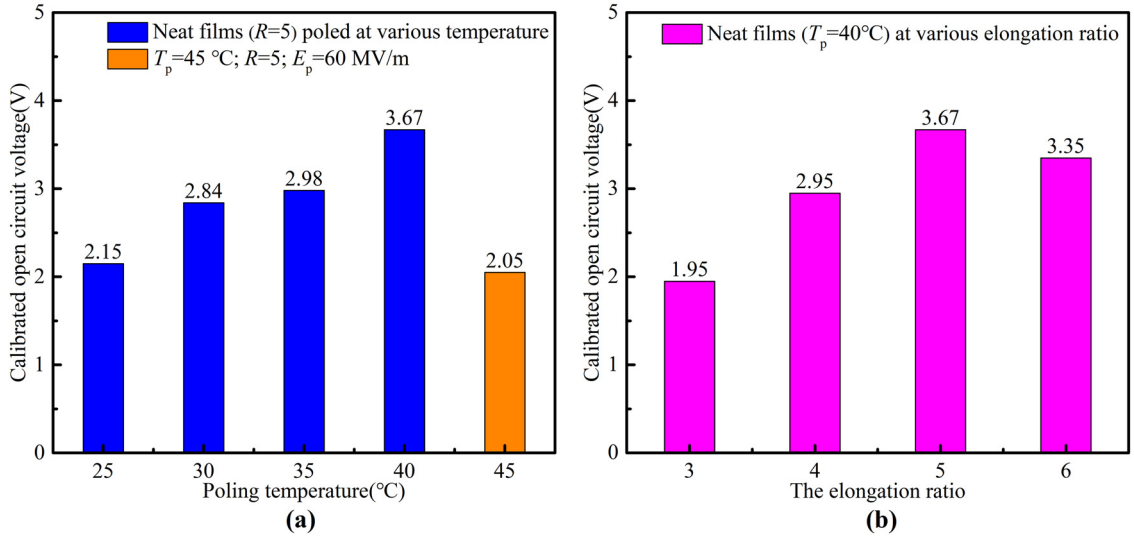

Figure 4: The calibrated open circuit output voltages of PVDF-HFP films: (a) PVDF-HFP films (R = 5) poled at various temperatures; (b) PVDF-HFP films (T_p = 40°C) stretched at various elongation ratios.

However, the alignment of molecular chains along the stretching direction continues when the elongation ratio increases from 4 to 5, which leads to better piezoelectricity. But more crystalline defects are formed when the elongation ratio increases further, which results in the reduction of piezoelectricity. The experimental results indicate that R = 5 and T_p = 40°C are the optimal parameters to produce high piezoelectric PVDF-HFP films.

3.2 FTIR

For PVDF-HFP films, FTIR is usually used to investigate the crystal structure. The α-crystal phase is the most common crystal phase in the initial crystallized films (non-stretched) with characteristic peaks of 489, 614, 766, 795, 855, and 976 cm^{-1} [31]. The characteristic peaks of the β-phase are at 510, 840, and 1,279 cm^{-1} [32]. The relative fraction of the β-phase $F(\beta)$ is an extremely important parameter in the preparation of PVDF piezoelectric films, which can be calculated by equation (2):

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

where K_α is 6.1×10^4 cm^2 mol^{-1}, K_β is 7.7×10^4 cm^2 mol^{-1}, and A_α and A_β are the areas of the absorption peaks near 766 and 840 cm^{-1}, respectively [7]. In this work, the integrating range is the peak (766 cm^{-1} for A_α and 840 cm^{-1} A_β) ± 10 cm^{-1}. For simplicity, the stretched films are denoted by S, and the stretched and poled films are denoted as SP.

Table 2: Relative fraction of β-phase $F(\beta)$ of PVDF-HFP films poled at various temperatures (R = 5)

T_p (°C)	25	30	35	40	45 (E_p = 60 MV m^{-1})
$F(\beta)$ (%)	87	96	96	97	92

Table 3: Relative fraction of β-phase $F(\beta)$ of PVDF-HFP films stretched at various elongation ratios (T_p = 40°C)

R	3	4	5	6
S (%)	61	74	80	76
SP (%)	68	93	97	96

$F(\beta)$ of untreated films (R = 1) is 14%.

As shown in Tables 2 and 3 and Figure 5, when the elongation ratio R is 5 and the maximum poling electric field E_{max} is 90 MV m^{-1}, almost only β-phase exists when the poling temperature is over 30°C. The $F(\beta)$ of samples poled at 45°C and 60 MV m^{-1} is slightly lower than other samples. During the poling process, the electric field forces the dipole moments to align along the electric field direction, and thus the piezoelectricity is improved. Besides, for the samples of lower $F(\beta)$, the induced stress by the electric field also promotes the α- to β-phase transformation to some extent. In Figure 5, the sample O (sample: R = 5, T_p = 45°C) contains a substantial α-phase. It is attributed to the transformation from γ to α phase at a

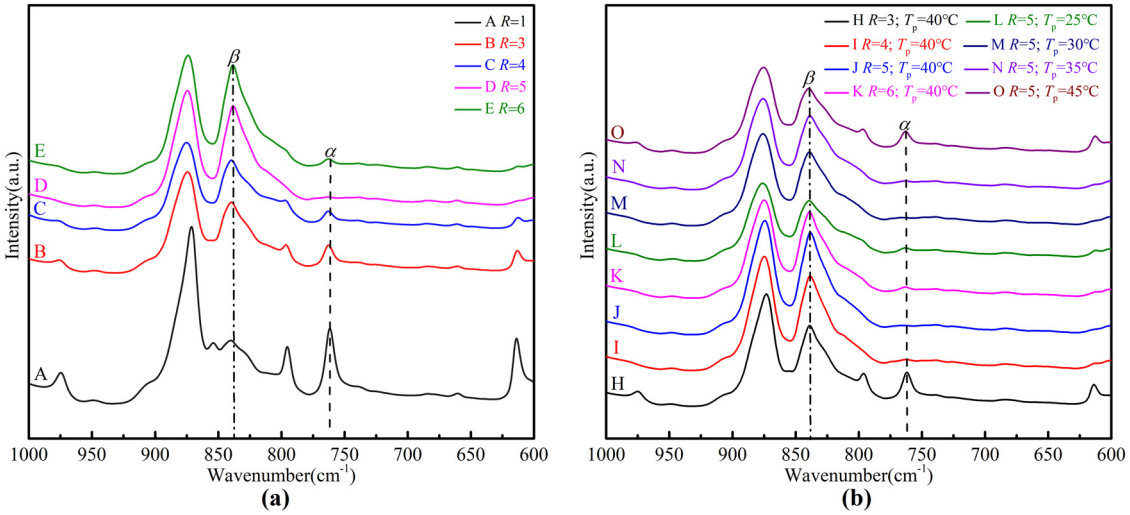

Figure 5: FTIR spectra of PVDF-HFP films: (a) stretched PVDF-HFP films at various elongation ratios. (b) Stretched and poled PVDF-HFP films at various elongation ratios (T_p = 40°C) or various poling temperatures (R = 5).

relative higher temperature. The relative lower electric field cannot increase the β-phase formation effectively [33]. When T_p is 40°C, R is 5, and E_{max} is 90 MV m^{-1}, the samples generate the highest open circuit voltages as shown in Figure 4, indicating the complete realignment of dipole moments compared to other samples.

Table 4: Characteristic angles of α-phase and β-phase in PVDF and its copolymers [38–40]

Crystal phase	Characteristic angles (plane)
α	17.8°(020), 18.4°(100), 20.0°(110), 26.6°(021)
β	20.4°(110,200), 36.3°

3.3 XRD

XRD was carried out by CuKα radiation with 2θ from 10° to 30° and the scan rate of 1° min^{-1}. The characteristic peaks of the α- and β-crystal phases in PVDF and their copolymers are shown in Table 4. It should be noted that little shifts of characteristic peaks may exist in different experiments. As shown in Figure 6, the characteristic

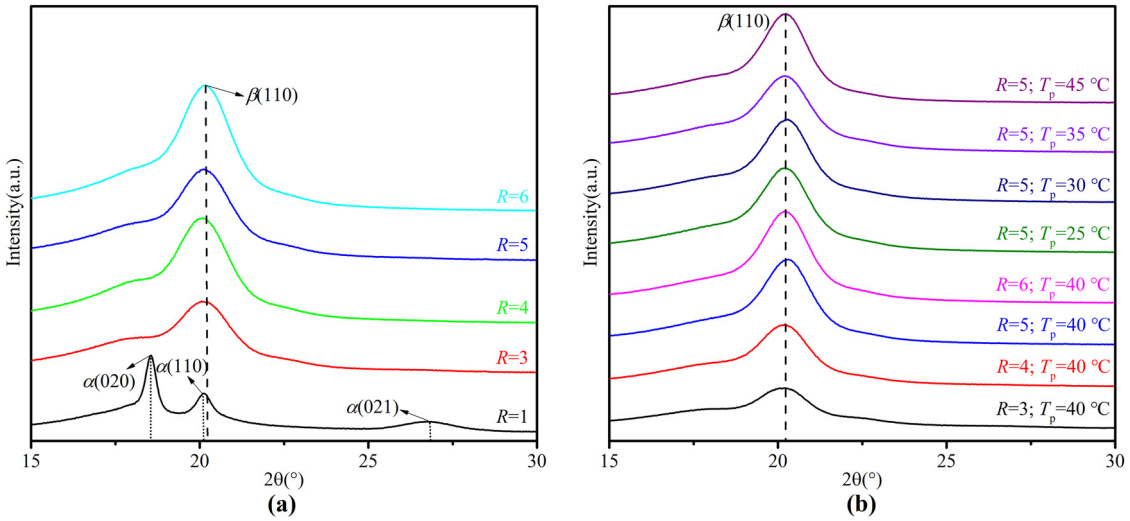

Figure 6: XRD diffraction spectrogram of PVDF-HFP films: (a) stretched plus poled films at various elongation ratios (T_p = 40°C) and various poling temperatures (R = 5); (b) stretched films at various elongation ratios.

Table 5: Crystallinity degree X_c of PVDF-HFP films poled at various temperatures (R = 5)

T_p (°C)	25	30	35	40	45 (E_p = 60 MV m^{-1})
X_c (%)	37	40	37	41	40

Table 6: Crystallinity degree of X_c of PVDF-HFP stretched films at various elongation ratios (T_p = 40°C)

R	3	4	5	6
S (%)	35	37	39	40
SP (%)	36	39	41	41

X_c of untreated films (R = 1) is 28%.

peaks of both α-phase and β-phase exist in the non-stretched samples. However, in the stretched samples, the characteristic peaks of the α-phase nearly disappear. Compared with the stretched films and poled samples, the spectra seem no obvious differences. Therefore, the α- to β-phase transformation mainly occurs in the stretching process. In the poling process, it is not so obvious since $F(\beta)$ is quite high in the stretched films. The main effect of poling is the realignment of the dipole moments in the PVDF-HFP matrix, and thus piezoelectricity can be obtained.

According to the experimental results, the characteristic peaks appear at 18.5°, 20.1°, and 26.7° in the films before stretching, which correspond to the plane of the α-phase, but the characteristic peaks of the β-phase are not obvious. It can be seen that the β-phase is dominant in the samples after stretching and heated-poling (Figure 6(b)). Combining with the FTIR results, it can be concluded that the stretching is the main factor for high β-phase, and poling can promote the α- to β-phase transformation in the samples of low $F(\beta)$. However, for high β-phase samples, it does little.

3.4 DSC

In the DSC process, the samples were cut into pieces of 3 mm^2 × 3 mm^2. The sample was first preserved at 40°C for 5 min and then heated from 40 to 200°C at a rate of 10°C min^{-1}. The following equation was used to calculate the crystallinity degree (X_c) of PVDF-HFP films [33]:

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

where ΔH_m is the melting enthalpy of the material which can be calculated by the DSC software, and ΔH_m^{ϕ} is the melting enthalpy of 100% crystalline PVDF-HFP, *i.e.*, 104.5 J g^{-1} [34].

The crystallinity degree of PVDF-HFP films is shown in Tables 5 and 6, and the DSC spectra are shown in Figure 7. It is observed that the crystallinity degree of the PVDF-HFP films increases after stretching, indicating that the concentration stress applied on the amorphous area can force the molecular chains to form crystal structure, which is consistent with the published data by Cai *et al.* [35]. While the X_c decrement was also reported [14],

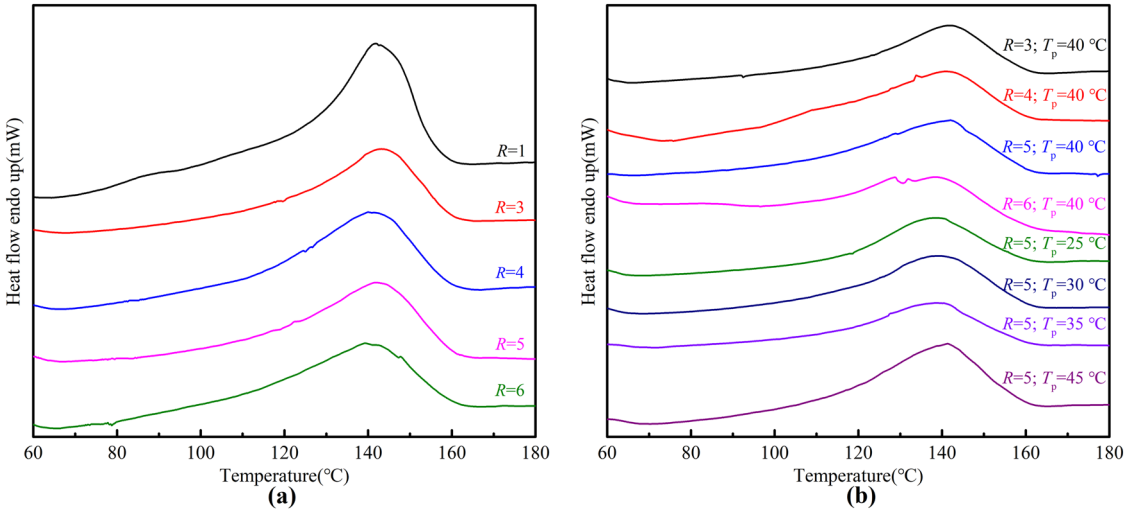

Figure 7: DSC thermograms of PVDF-HFP films: (a) stretched PVDF-HFP films at various elongation ratios; (b) stretched plus poled PVDF-HFP films at various elongation ratios (T_p = 40°C) and various poling temperatures (R = 5).

for higher draw ratios the polymer chains become more oriented, which results in the phase transformation accompanied by a decrease of the crystallinity degree. It reflects that the influence of stretching on crystallinity is complicated. In this work, the increase of X_c is attributed to the stress work on the amorphous area which forces part of the molecular chains to align in the β-phase. On the other hand, crystallization defects may arise during the stretching process [36,37]. From Table 6, the crystallinity degree changes little after poling, indicating it works little on the crystallinty degree, because it cannot provide enough stress on the molecular chains in the amorphous region to form crystal structure [28]. The main effect of poling is the realignment of dipole moments, as reflected by the change of the open circuit voltage.

4 Conclusion

In this study, the influences of poling temperature and elongation ratios on phase transformation and output voltages of PVDF-HFP films are investigated. The FTIR and XRD spectra demonstrate that the α- to β-phase mainly occurs in the stretching process ($R \geq 3$) due to molecular chain elongation caused by the external force. The poling temperature has strong effects on the piezoelectricity of PVDF-HFP films. It is found that the output open circuit voltage increases with the temperature until 40°C. While the temperature is 45°C, the poling fails when the electric field is over 60 MV m^{-1}. Thus, the piezoelectricity cannot be further increased. The optimal parameters are defined as R = 5, T_p = 40°C, and E_{max} = 90 MV m^{-1}. At this condition, the open circuit voltage reaches 3.67 V, 71% higher than that of samples poled at 25°C. The experimental method of heated-poling reported in this study is facile and of low cost for preparing efficient piezoelectric films.

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Data availability statement: The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

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