In-situ polarization enhanced piezoelectric property of polyvinylidene fluoride-trifluoroethylene films

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Abstract: The polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) piezoelectric film was obtained by the in-situ polarization, which 10x increased the piezoelectric coefficient d₃₃. By using our polarizing system, the PVDF-TrFE film can be polarized in 5 minutes at room temperature. Compared with the traditional polarization method, the in-situ polarization was performed with low poling voltage, short poling time, and can ensure the obtained PVDF-TrFE film with enhanced piezoelectric performances and uniform distribution among large area. The results provide a new method for PVDF-TrFE films with large area and high piezoelectric coefficient, which improves the piezoelectric performance and broadens the application in energy harvesting.

1. Introduction
The polymer piezoelectric materials have many advantages such as low density, low impedance, and high piezoelectric coefficient. It has quickly become the attention of many developers. One of the most representative is the poly(vinylidenedifluoride-trifluoroethylene) (PVDF-TrFE). The piezoelectricity allows it to convert the ambient mechanical stimulations to electricity, which has been widely used in energy harvesting applications such as the piezoelectric nanogenerators (PENGs)[1-4]. With rapid development of smart wearable devices and the energy conversion efficiency, it’s vital to improve the piezoelectric properties of PVDF so as to improve its value in the smart wearable devices applications. The piezoelectricity of PVDF origins from its crystalline structures. As a semi-crystalline polymer, PVDF presents a complex crystalline structure and crystalline phases (commonly α-, β-, and γ-)[5-7]. The non-polar α-phase has a TGTG chain conformation resulting in the self-cancelation of dipoles. The β-phase has an all trans (TTTT) planar zigzag with the strongest polarity, while the γ-phase display a T₃GT₃G chain conformation which is partial polar. By thermal treatment [8-10] or poling under a high electric field (150kV/mm), the α-phase can be transformed into the γ-phase or β-phase. In order to increase the β-phase synchronous decrease the α-phase crystallinity, many methods have been developed in the preparation of PVDF materials[11]. Copolymers of PVDF such as PVDF-TrFE have been synthesized to achieve an intrinsic β-phase crystal. In the study, large area of 200×200 mm of PVDF-TrFE film with enhanced piezoelectric coefficients were prepared by in-situ polarization. Compared with the traditional methods, the in-situ polarization has much shorter processing time. The prepared PVDF-TrFE films have great distribution uniformity with good piezoelectric performance.
2. Experiment

2.1. Materials
PVDF-TrFE (FC20, Piezotech SAS, France), methyl ethyl ketone (MEK, 99.5%, KESHI, Chengdu, China).

2.2. Methods
The PVDF-TrFE copolymer powder (70:20) and the methyl ethyl ketone solution were mixed at a mass ratio of 1:8.5 to obtain a PVDF-TrFE solution and stirred by a magnetic stirrer for 6h. Then, 3ml of the solution was slit coated on the glasses and were transferred to a vacuum plate to evaporate the solvent and form the PVDF-TrFE films with thickness of 20μm. These films were further annealed at 140℃ for 0.5h. Subsequently, the PVDF-TrFE films were in-situ poled by a laboratory-made equipment. The preparation process was shown in figure 1.

![Preparation process of PVDF-TrFE films](image)

Figure 1. The preparation process of PVDF-TrFE films

To investigate the piezoelectric coefficients of the PVDF-TrFE sample, piezoelectric tester (d33 METER, YE2730A, APC) was introduced. X-ray diffraction (XRD) was carried out on a D/Max2500 VB2t/PC X-ray diffractometer (Rigaku, Japan) with a Cu target radiation for a 2θ range of 5-50° at an angular resolution of 0.5°. The morphology of the PVDF-TrFE films were observed by a field-emission scanning electron microscope (SEM, S-3400, Hitachi).

3. Result and discussion
The laboratory-made polarization equipment is primarily consisted of source, grid and rotated stage. Figure 2 shows the schematic diagram of the in-situ polarization process used in the study. After the source and grid move above the sample, a voltage of 7.5kV was applied on the source electrode to generate electronegativity ions, then, these electronegativity ions were accelerated by the grid with voltage of 3.0 kV and deposited on the surface of the sample evenly, as shown in figure 3 the rather close distance (equal to the thickness of film, 15μm) between the virtual electrode formed by the electronegativity ions and the bottom electrode can generate a tremendous electrical field which leads to an effective polarization. During the poling process, the substrate rotated for 360° slowly which ensures the uniformly piezoelectricity of the PVDF-TrFE coatings.
Figure 2. Schematic diagram of in-situ polarization

Figure 3. Piezoelectric coefficient corresponding to different polarization spacing and polarization voltage
Table 1. Comparation of d33 of PVDF-TrFE films after different processing stage

| Item     | d33/ pC/N |
|----------|-----------|
| Drying   | 0         |
| Annealing| 2         |
| Poling   | 25        |

After the in-situ polarization, the piezoelectric coefficient (d33) of PVDF-TrFE film are tested and the result are shown in table 1. The PVDF-TrFE films shows rather low piezoelectricity (d33=0 pC/N) after drying in the oven. The value of d33 improved slightly to 2.5pC/N after the PVDF-TrFE films annealed in 140°C for 1h due to the heat treatment induced the formation of β-phases crystal. After poling, the PVDF-TrFE film showed dramatically enhanced piezoelectric coefficient of d33=25 pC/N. Then the piezoelectric property increased slightly after 2 days from 25pC/N to 28pC/N with excellent distribution.

The crystalline properties of PVDF-TrFE before polarization and after polarization were characterized by XRD as provided in figure 4. In figure 4, the XRD patterns show that when the PVDF-TrFE films after drying, two peaks at 18.27° and 20.12° were observed. The peak at 20=18.27° is corresponding to the (100) crystal planes of the α-phase. Meanwhile, the γ-phase is present at superposition point of the peaks located at 18.5°associated with (020) crystal planes. The sharp peak at 20.12° represents the Bragg diffraction of (110)/(200) of β-phase and is from the ferroelectric β-phase having all-trans conformation. After annealing at 140°C for 1h, the only sharp peak at 20.12° which referred to the ferroelectric β-phase became more distinct. There were two extremely weak and broad peaks at 2θ= 35.51° and 40.91°which indicates a highly preferred orientation for the PVDF-TrFE films. And the phenomenon that the peak at 2θ=18.27°vanished indicates that γ-phase disappeared in the high temperature. The distinct β-phase peak was also found in the PVDF-TrFE films after poling process.

Figure 4. XRD patterns of PVDF-TrFE films before polarization (a) and after polarization (b)

In figure 5 before polarization at 140°C for 1h, the PVDF-TrFE films (figure 5(a)) showed a lot of grains which were composed of randomly distributed 200-300 nm rod-like crystallites. This is a typical characteristic of β-phase PVDF-TrFE. It has been reported that the content of TrFE can influence the crystalline polymorphs of PVDF-TrFE. When the PVDF-TrFE content in TrFE is over 20
mol%, it can directly form the β-phase crystal. The image of PVDF-TrFE after poling (figure 5(b)) showed more distinct grain than that of the PVDF-TrFE films after annealing. This proves the in-situ polarization process leads a dramatic improvement of the formation of β-phase crystal in PVDF-TrFE films.

Figure 5. SEM images of PVDF-TrFE before polarization (a) and after polarization (b)

4. Conclusions
In the study, PVDF-TrFE films with uniform distribution and high d33 coefficient of 25±2 pC/N were prepared by in-situ polarization. The XRD results proved the in-situ polarization can promote the transition from α-phase crystal to β-phase crystal and the formation of β-phase crystal in PVDF-TrFE film, which will further improve its piezoelectricity. Thus, the easy processing and the excellent and uniform d33 value of PVDF-TrFE films make the in-situ polarization great potential in piezoelectric materials processing methods.

Reference
[1] Li, C., Wu, P.M., Lee, S. (2008) Flexible dome and bump shape piezoelectric tactile sensors using pvdf-trfe copolymer. J. Microelectromech. S., 17(2): 334-341.
[2] Dargaville, T.R., Elliott, J.M., & Celina, M., (2010) Evaluation of piezoelectric pvdf polymers for use in space environments. iii. comparison of the effects of vacuum uv and gamma radiation. J. Polym. Sci., Part B: Polym. Phys., 44(22): 3253-3264.
[3] Serrado-Nunes, J., Kouvatov, A.Z., V Müller, Beige, H. (2006) Piezoelectric and optical response of uniaxially stretched (vdf/trfe) (75/25) copolymer films. Mater. Sci. Forum., 514-516, 945-950.
[4] Bettington, M., Walker, N., Brown, I. (2014) A clinicopathological and molecular appraisal of a large series of traditional serrated adenomas. IEEE Sens. J., 13(6): 2237-2244.
[5] Zhang, Q., Liu, S., Luo, H. (2020) Hybrid capacitive/piezoelectric visualized meteorological sensor based on in-situ polarized pvdf-trfe films on tft arrays. Sens. Actuators, A Phys., 315: 112286.
[6] Khajavi, R., Abbasipour, M. (2016) Piezoelectric PVDF Polymeric Films and Fibers: Polymorphisms, Measurements, and Applications. Springer International Publishing.
[7] Robinson, H.C., Kavarnos, G.J., Holman, R.W., (1997) Calculations of the elastic compliance and piezoelectric constants of pvdf and p(vdf-trfe) crystals using molecular mechanics. J. Acoust. Soc. Am., 102(5): 3106.
[8] Nguyen, V., S., Strashilov, V., Alexieva, et al. (2015) Structural impact on piezoelectricity in pvdf and p(vdf-trfe) thin films. Appl. Phys. A. Mater., 118(4): 1469-1477.
[9] Wang, Y., Neese, B., Zhang, Q. M. (2007) P6h-10 high piezoelectric responses in p(vdf hfp)
copolymers for sensors and transducers. Pro. IEEE Ultrasonics Symp., 2606-2609.

[10] Hu, X., Ding, Z., Fei, L. (2019) Wearable piezoelectric nanogenerators based on reduced graphene oxide and in situ polarization-enhanced pvdf-trfe films. J. Mater. sci, 54(8), 6401-6409.

[11] Da Rgaville, T. R., Celina, M., Chaplya, P.M. (2010) Evaluation of piezoelectric poly (vinylidene fluoride) polymers for use in space environments. i. temperature limitations. J. Polym. Sci., Part B: Polym. Phys., 43(11): 1310–1320.