Crystallization behavior and electroactive properties of PVDF, P(VDF-TrFE) and their blend films

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Abstract

PVDF, poly(vinylidene fluoride), as a semi-crystalline polymer, has interesting electroactive properties but usual melt and solution processing techniques result in its thermodynamically favored non-polar α -phase. By comparison, poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE), PT for short, directly crystallizes in the polar β -phase under the same conditions as PVDF. In this study, blend thin films comprising PVDF and P(VDF-TrFE) were prepared by solvent casting method. The difference in the crystallization behavior is comprehensively investigated between the polymers: PVDF, P(VDF-TrFE), and the resulting blend films. It is found that replacement of the fluoride atom in TrFE monomer induces a strong steric hindrance that may alter the crystallization process to become more favorable for nucleation of the PVDF β -phase. To figure out the effect of TrFE content on the crystallization behavior and electroactive properties, films with different blend ratios of PVDF and P(VDF-TrFE) were prepared. We found that the PVDF films exhibit higher crystallization activation energy (ΔE) as PT content increases. The atomic force microscopy (AFM) in the piezoresponse force microscopy (PFM) mode illustrated that P5T5 films with equal contents of PVDF and P(VDF-TrFE) induced the highest d_{33} values.

Keywords: Poly(vinylidene fluoride), Poly(vinylidene fluoride-Trifluoroethylene), crystallization, piezoelectric materials

1. Introduction

Poly(vinylidene fluoride) (PVDF) and its copolymers are widely used as polymeric ferroelectric materials in numerous applications due to their excellent piezoelectric, pyroelectric, and ferroelectric properties [1]. As a semi-crystalline polymer, PVDF shows a complex structure comprising at least five crystalline phases (α -, β -, γ -, δ - and ϵ -phase) [2]. The α - and β -phases are considered as the most common forms having distinct electrical properties. The β -phase has the largest spontaneous polarization due to the trans-planar zigzag conformation (TTTT), whereas α -spherulites (trans-gauche conformation, TGTG) are the thermodynamically favorable forms with non-polar crystalline phases [3]. Hence, various approaches were developed to obtain the polar β -phase while suppressing the non-polar α -phase in PVDF materials. A number of effective methods have emerged, including electrospinning [4], film-casting via polar solvents [5], uniaxial or biaxial drawing [6], supercritical carbon dioxide [4], quenching and poling of the film [7], rapid thermal treatment, and incorporating with nanoparticles [8-10]. Moreover, different copolymers, such as poly(vinylidene fluoride-trifluoroethylene) and P(VDF-TrFE), have been developed to improve the β -phase of PVDF [11, 12].

Compared with PVDF, P(VDF-TrFE) is the most studied PVDF copolymer. It exhibits elevated remnant polarizations, which give rise to larger electromechanical coupling factors. This, in turn, yields higher transformation efficiencies from mechanical to electrical [13]. P(VDF-TrFE) has a Curie Temperature (T_c) lower than its melting temperature (T_m), which can vary from 55 to 128 °C, depending on the amount of TrFE [14]. The extra TrFE monomers introduced into PVDF chains can change the crystallization behavior of PVDF films [15]. Recent studies reported that P(VDF-TrFE) can directly be crystallized into the polar β -phase when the TrFE content is higher than 20 mol%, regardless of the fabrication method and conditions [16]. The Density Function Theory (DFT) simulations revealed that the β -phase is easier to obtain in P(VDF-TrFE) because β -conformation is more thermodynamically stable than the α -conformation, which makes the transition from β to α more difficult

[17].

One of the limitations for both the PVDF and P(VDF-TrFE) ferroelectric polymer materials is their low piezoelectric coefficient (d_{33}), which is directly related to the crystallinity of the materials [18]. Thus, in-depth understanding on the crystallization behavior is required to gain better insights. In this work, neat PVDF and P(VDF-TrFE) films, as well as blending films of PVDF and P(VDF-TrFE) with different blending ratios were prepared. The differential scanning calorimetry (DSC) cooling scan at different scan rates was used as crystallization dynamics method to assess the crystallization activation energy and the effective energy barrier (ΔE) of the samples. The electroactive properties of all samples were also investigated by atomic force microscopy (AFM) using a piezoresponse force microscope model.

2. Experimental

2.1. Materials and methods

All materials were used without further purification and were purchased from the following companies: PVDF (F401, Changzhou Resin Corp, China), P(VDF-TrFE) (PT hereinafter, 70/30 mol%, Piezotech S.A.S, Hesingue, France), and N, N-dimethylformamide (DMF, 99.5%, Guangfu Fine Chemical Research Institute, Tianjin, China).

Neat PVDF films were fabricated by solution casting, where PVDF (0.6 g) was first dissolved in 12 mL DMF solvent and left under constant stirring for 6 h at the ambient temperature. A volume of 10 mL of the solution was poured into a glass petri dish. To initiate the crystallization process, the resulting mixtures were further annealed at 90 °C in vacuum for 20 h. To gain better insights into the crystallization behavior of PVDF and PT, neat PT films and a series of blend films of PVDF and PT were prepared under the same conditions. Three blend films were prepared using mass ratios (w/w, PVDF/PT): P9T1 (9/1), P5T5 (5/5), and P1T9 (1/9). The morphological features were studied by adding 2 mL of all solutions into self-made aluminum cells ($2 \times 2 \text{ cm}^2$) followed by annealing at 100 °C under vacuum for 2 h.

The resulting films were then subjected to a polarized optical microscope.

2.2. Characterization

A Fourier transform infrared spectrometer (Vertex 70, Bruker Optics, Germany) in the ATR model and an X-ray diffractometer (XRD, XD-3, PERSEE, China) with CuK α radiation ($\lambda = 0.1541$ nm) were used to measure the crystallization behavior of the samples. The lamellar structures were measured using a small-angle X-ray scattering (SAXS) instrument (SAXSess mc2, Anton Paar, Austria) equipped with a Kratky block-collimation system and a 3 kW ceramic tube as the X-ray source. The X-ray wavelength was set to 1.542 Å and a CCD with an image intensifier was used as a detector. To test the nonisothermal crystallization, differential scanning calorimetry (DSC) measurements were conducted on a Q2000 differential scanning calorimeter (TA Instruments, New Castle, DE, USA) with a nitrogen purge of 50 mL min⁻¹. The surface morphologies of the samples were collected by a polarized optical microscope (POM) (PM6000, Jiangnan Novel, China) and an atomic force microscope (AFM, NT-MDT Corp, Russia). The piezoelectric coefficients (d_{33}) were tested by AFM in PFM mode.

3. Results and discussion

The POM micrographs of films based on PVDF, P5T5, and PT are shown in Fig. 1. It can be seen that neat PVDF exhibits large numbers of spherulites with the typical Maltese crosses (Fig. 1a). The number of spherulites dramatically decreased for P5T5 and only a few of them depict Maltese crosses. The POM image of PT, however, does not show any spherulites, indicating that the amorphous TrFE chains can impede the continuous growth of crystals in PVDF [19]. The POM images of P9T1 and P1T9 are presented in Fig. S1. The morphologies look pretty similar to those of P5T5 and PT, respectively.

Fig. 1. POM images of PVDF (a), P5T5 (b) and PT (c).

It has been reported that TrFE content can influence the crystalline polymorphs of PT, which can directly be crystallized in the β -phase, if PT content in TrFE is over 20 mol% [20]. By comparison, the crystallization of PVDF films prepared through solution-casting leads to both α and β -phases coexisting together [21].

The crystalline phase of films based on neat PVDF, P9T1, P5T5, P1T9 and PT, were further characterized by FT-IR and XRD (Fig. 2). The peaks at 614 cm^{-1} and 764 cm^{-1} related to the α -phase have emerged in PVDF films and practically vanished for other samples (Fig. 2a). By contrast, films based on P9T1, P5T5, P1T9 and, PT are β -phase dominant, exhibiting characteristic absorption bands at 510 cm^{-1} , 840 cm^{-1} , and 1175 cm^{-1} [22]. It should be noted that the absorption band at 840 cm^{-1} can also be assigned to the γ -phase. Therefore, in order to rule out the existence of γ -phase, it is necessary to look at the absorption band located at 1234 cm^{-1} peculiarly assigned to the γ -phase [23]. The results show that the peak at 1234 cm^{-1} emerges in the spectra of PVDF, P9T1 and P5T5 films, but nearly absent in both the P1T9 and PT films. This suggests that the crystalline α , β - and γ -phases are coexisting in PVDF. However, as PT content increases, the crystalline phase of blend films turn to β - and γ -phases, and finally induce β -phase as the dominant form in the PT films.

Fig. 2. FT-IR (a) and XRD (b) spectra of neat PVDF, P9T1, P5T5, P1T9 and PT films.

The FT-IR data were further confirmed by XRD shown in Fig. 2b. The PVDF depicts two diffraction peaks at $2\theta = 18.3^\circ$ and 19.9° , corresponding to the (100) and (110) crystal planes of the α -phase, respectively. Meanwhile, the γ -phase is present at superposition point of the peaks located at 18.5° and 20.0° associated with (020) and (110) crystal planes [24]. Based on the FT-IR measurements, albeit PT and all other blend films showed same diffraction peaks around 18.3° and 19.9° , more likely attributed to the γ -phase. The peak at $2\theta = 20.4^\circ$, corresponding to (110) and (200) reflection of the β -phase, becomes more distinct in both the P9T1 and PT films [25]. The latter clearly indicates that higher PT contents are beneficial to the formation of the β -phase, consistent with the FT-IR data.

Fig. 3. The second heating curves (a) and Kissinger plots (b) of PVDF, P9T1, P5T5, P1T9 and PT samples.

The crystallization behavior of the films based on PVDF, P9T1, P5T5, P1T9 and PT were analyzed by DSC scans and the data are presented in Fig. 3. The incorporation of PT component clearly shifts the melting temperature of PVDF downwards, from ~ 161 °C of PVDF to ~ 148 °C of PT (Fig. 3a). It is noteworthy that P5T5 exhibits two melting peak temperatures that could be ascribed to differences in the lamella thicknesses between samples [26]. The reason for that has to do with: 1) the β -phase presents a melting temperature similar to that of the α -phase, and 2) the proportion of the α - and β -phase are higher than that of the γ -phase for all samples as shown by FT-IR [4]. Hence, the shift in the melting temperatures is more likely to be caused by differences in the lamella thicknesses rather than by the difference in the crystalline phases. This suggests that increased PT content would lead to decreased lamella thicknesses.

The enthalpies of fusion (ΔH_m) and degrees of crystallinity (X_c) of all samples are listed in Table 1 and the detailed calculation of ΔH_m and X_c are given in SI part.

Table 1 The enthalpies of fusion, crystallinity and effective energy barrier of PVDF, P9T1, P5T5, P1T9 and PT films

	ΔH_m (J g ⁻¹)	X_c (%)	ΔE (kJ mol ⁻¹)
PVDF	30.9	31.5	-348.2
P9T1	31.9	31.4	-470.6
P5T5	28.8	29.8	-605.9
P1T9	22.3	24.3	-722.1
PT	21.8	24.1	-734.9

For polymer systems, the crystallization activation energy or the effective energy barrier (ΔE) can roughly be used to estimate the growth in crystal nucleus. Considering the variation of the crystallization peak temperature (T_p) as a function of the cooling rate (ϕ), ΔE can be derived from the Kissinger model using eq. (1):

$$\ln \left(\frac{\phi}{T_p^2} \right) = \text{constant} - \frac{\Delta E}{RT_p} \quad (1)$$

where R represents the universal gas constant [27].

Fig. 3b shows the plots of $\ln(\phi/T_p^2)$ versus $1/T_p$. It can be seen that the plots of all samples present a good linear relationship. The dynamic crystallization curves are shown in Fig. S2 and the ΔE values of neat PVDF, P9T1, P5T5, P1T9, and PT films are listed in Table 1. The negative ΔE values indicate that the crystallization rate of all samples increased as temperature reduced. In addition, the films with more PT content show higher ΔE values, suggesting that the strong steric hindrance caused by fluoride atom can hinder the crystallization process and hence enable more favored β -phase nucleation of PVDF [28].

Moreover, the temperatures of Curie transition, which are about 96 °C, showed minor changes for PT, P1T9, and P5T5 films, but absent for P9T1 and PVDF films. The PT films depicted the highest values of enthalpies of Curie transition and decreased gradually for P1T9 and P5T5. One possible reason for this observation is that fluoride atom with larger volumes replaced the hydrogen atom with smaller volumes which bring about a strong steric hindrance. As a consequence, higher contents PT would require more energy for bond rotation to convert into the non-ordered paraelectric phase [29].

Fig. 4. I - q curves collected by SAXS of PVDF, P9T1, P5T5, P1T9 and PT samples.

SAXS was conducted in order to elucidate the lamellar structure of all samples and the results are presented in Fig. 4. It will be noted that the peaks undergo a shift towards higher q values and appear broadened as PT content rises. The L_w (long period), L_c (crystalline layer thickness), and L_a (amorphous layer thickness) can be calculated using the peak maxima listed in Table 2 [30].

$$L_w = 2\pi/q_{max} \quad (2)$$

$$L_c = L_w \times X_c \quad (3)$$

The L_w , L_c and L_a values gradually reduce as PT content increases, which intrinsically could be attributed to the strong steric hindrance caused by the fluoride atom. This, in turn would lead to the hindered movement of the molecular chains during the crystallization process. Meanwhile, the amorphous TrFE chains located in the regimes between the PVDF lamella and/or crystal stacks are excluded from the PVDF lamella to impede continuity of the PVDF crystalline phase [26].

Table 2 SAXS Parameter for PVDF, P9T1, P5T5, P1T9 and PT samples

	L_w (nm)	L_c (nm)	L_a (nm)
PVDF	27.3	8.6	18.7
P9T1	23.3	7.3	16.0
P5T5	19.3	5.8	13.5
P1T9	15.3	3.7	11.6
PT	12.8	3.1	9.7

The surface morphologies of PVDF, P9T1, P5T5, P1T9, and PT films were scanned by AFM and the results are presented in Fig. 5. The PVDF films presented a morphology consisting of spherulites (Fig. 5a) whereas PT displayed a flat surface with scattering micropores. As PVDF content rises, the morphology of P1T9, P5T5, and P9T1 films converted from porous into features dominated by spherulite, which is tentatively due to the molecular chains of PT that require more energy to move during the crystallization process, leading to the formation of flat surfaces with pores caused

by evaporation of the solvents [31]. In contrast, the molecular chains of PVDF can move more easily to yield a surface morphology dominated by spherulite [32]. The piezoelectricity (d_{33} , piezoelectric coefficients) of the samples is assessed by AFM in the PFM model, where all d_{33} values are presented by the average of 5 measurements (see Fig. S3). The d_{33} values of neat PVDF, P9T1, P5T5, P1T9, and PT are 25.0 ± 2.0 , 27.3 ± 4.7 , 51.2 ± 5.0 , 44.3 ± 8.4 and 35.9 ± 6.7 pmV⁻¹, respectively. This result could be tentatively ascribed to two aspects. First, both PVDF and P9T1 samples are α , β - and γ -phases coexisted. Thus, the increase in the non-polar α phase could result in the decreasing of d_{33} values. And second, although β -phase is the dominant form in P5T5, P1T9, and PT films, but the gradual decrease in the total crystallinity will accordingly bring the decrease in d_{33} values.

Fig. 5. AFM images and 3D images of PVDF (a), P9T1 (b), P5T5 (c), P1T9 (d) and PT (e)

samples.

4. Conclusions

The crystallization and the piezoelectricity of PVDF, P(VDF-TrFE) and their blend films were investigated. The results revealed that as PT content increases, the PVDF films exhibit higher crystallization activation energy (ΔE), suggesting that TrFE monomers could hinder the crystallization caused by the strong steric hindrance from the fluoride atom. As a consequent, when compared with other samples, PT films with dominant β -phase had the lowest degrees of crystallinity and crystalline lamella thickness. Furthermore, the piezoelectricity measurements from AFM at the PFM mode displayed that the P5T5 films have the highest d_{33} values. We believe that these findings would be beneficial for understanding the polymer crystallization processes and find alternatives to improve the piezoelectricity of fluoro-polymers.

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