

## EFFECT OF CRYSTALLINITY ON POLARIZATION FATIGUE OF FERROELECTRIC P(VDF-TrFE) COPOLYMER FILMS\*

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**Abstract** The dependence of polarization fatigue on crystallinity of vinylidene fluoride and trifluoroethylene copolymer films was studied. Experimental data indicated that the higher the crystallinity of the film was, the slower the fatigue rate of the film became. A possible explanation was put forward, and it was regarded that the space charges, trapped at the boundaries of crystallites and/or captured by the defects lying both in amorphous and crystalline phases, should make the major contribution to polarization fatigue.

**Keywords:** Polarization fatigue; Ferroelectric polymer; Crystallinity.

### INTRODUCTION

Since the discovery of ferroelectric and piezoelectric properties of poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene [P(VDF-TrFE)]<sup>[1, 2]</sup>, many studies have been focused on ferroelectric polymers due to their widespread applications in transducers, sensors and actuators and a potential use in high-density data storage<sup>[3]</sup>. Recently, electronic devices based on these ferroelectric polymers have also been realized, such as non-volatile memory elements<sup>[4]</sup>, organic field-effect transistors (OFETs)<sup>[5]</sup> and so on.

Polarization fatigue, which is defined as a reduction of the observed polarization with repeated cycling of the applied electric field, is one of the most dominant factors which have restricted the applications of ferroelectrics. Considerable studies on polarization fatigue of inorganic ferroelectric materials have been carried out, and it is well known that the fatigue phenomenon is caused by space charge or domain boundary effects<sup>[6]</sup>. Polarization fatigue can also be observed in ferroelectric polymers<sup>[6, 7]</sup>, but these films are semicrystalline with coexistence of crystalline phase and amorphous phase and have a more complex morphology than that of the conventional single crystal or ceramic ferroelectrics. Therefore, whether the ferroelectric polymers have the similar origin of fatigue as that of the inorganic ferroelectrics is still a question, and seldom studies on this issue have been reported. In our previous work<sup>[7]</sup>, we have investigated the polarization fatigue in P(VDF-TrFE) thin films and found that the fatigue rate depended on frequency, amplitude, waveform and polarity of the applied driving voltage. However, the physical properties of ferroelectric polymers such as the degree of crystallinity should also be a key factor on polarization fatigue, and there are no related studies that have been reported before. In this paper, we report the dependence of polarization fatigue on the crystallinity of P(VDF-TrFE) copolymer films, which can be controlled by heat treatments at different temperatures.

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## EXPERIMENTAL

### Preparation of Films

Copolymer films were prepared by spin-coating method from a 5.0 wt% solution of 72/28 P(VDF-TrFE) in butanone on cleaned glass slides. The films had a thickness of *ca.* 550 nm measured by Surfcoater ET 3000 (Kosaka Laboratory Ltd., Japan). The Curie temperature of such films was *ca.* 122°C, and the melting temperature was *ca.* 150°C obtained from the phase diagram<sup>[8]</sup>. The as-deposit films were annealed at 120°C, 140°C and 155°C respectively for 8 h to obtain different crystallinity. Both top and bottom Al electrodes (about 30 nm thick) were vacuum evaporated on the films, and the formed sandwich structure<sup>[9]</sup> was prepared for fatigue measurements.

### Characterization of Films

X-ray diffraction (XRD) analysis of copolymer films annealed at various temperatures was used to obtain the information of crystallinity, and it was carried out by X'Pert Pro (PANalytical, Holland). Morphological changes of copolymer films were imaged using an atomic force microscope (AFM) Nanoscope IIIa (Digital Instruments, USA). Comparison of ferroelectric properties of different films was performed with the ferroelectric switching current response which was recorded by a homemade Sawyer-Tower circuit.

### Tests of Polarization Fatigue

Hysteresis loops were acquired by integrating the current response during ferroelectric switching processes. The fatigue tests of films were carried out by applying an alternating triangular voltage with amplitude of 40 V and frequency of 100 Hz. This fatigue voltage was high enough to cause ferroelectric switching. The fatigue process was interrupted at pre-calculated intervals to monitor the hysteresis loop with a triangular voltage of the same amplitude, but at a frequency of 1 Hz. For more details on polarization fatigue measurements one could refer to Ref. [7].

## RESULTS AND DISCUSSION

The XRD patterns (as shown in Fig. 1) of P(VDF-TrFE) thin films annealed at various temperatures were used to analyze the crystallinity. Characteristic peaks, attributed to  $\beta$ -phase of P(VDF-TrFE) copolymer films<sup>[10, 11]</sup>, appeared at *ca.* 20° (2 $\theta$ ). According to Ref. [12], the diffraction curve could be separated into a crystalline peak and an amorphous peak, and the ratio of the integral of the crystalline diffraction intensity over the total coherent scattering could be considered as the degree of crystallinity. The calculated degree of crystallinity of P(VDF-TrFE) films is listed in Table 1. The as-deposit (non-annealed) copolymer films consisted mainly of the amorphous phase, and their crystallinity was only 25% in our experiments. The diffraction peak was enhanced with increasing annealing temperature, and the films annealed at 140°C reached the highest degree of crystallinity (91%). However, reaching up to 155°C, the films were melted (melting point was about 150°C<sup>[8]</sup>) and recrystallized to a relatively low crystallinity (52%).

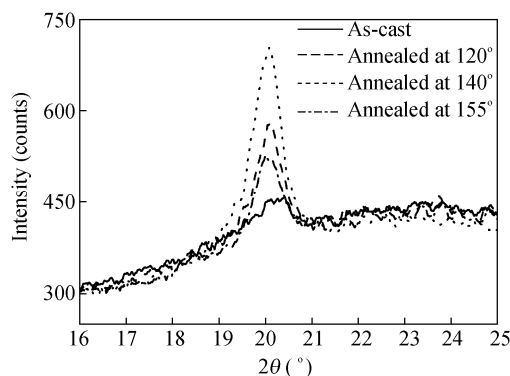


**Fig. 1** XRD patterns of as-deposit P(VDF-TrFE) thin films and the films annealed at 120°C, 140°C and 155°C, respectively

**Table 1.** The degree of crystallinity of P(VDF-TrFE) films

| Annealing temperature   | As-deposit | 120°C | 140°C | 155°C |
|-------------------------|------------|-------|-------|-------|
| Degree of crystallinity | 25%        | 68%   | 91%   | 52%   |

The degree of crystallinity of P(VDF-TrFE) copolymer films could be known from XRD analysis<sup>[12, 13]</sup> or from the measurements of local butterfly loops<sup>[14]</sup>. The as-deposit (non-annealed) copolymer films consisted mainly of the amorphous phase, and their crystallinity only reached values of *ca.* 30% at most from XRD data<sup>[12, 13]</sup> or 10% estimated by the butterfly loops<sup>[14]</sup>. Films annealed just below the Curie point obtained a little higher crystallinity which was about 60% from butterfly loop measurements<sup>[14, 15]</sup>, while a proper annealing treatment at the temperature between the Curie point and the melting point could lead to a dramatic increase of the crystallinity up to a maximum of 95%<sup>[12–14]</sup>. Our XRD results are well consistent with those previous works. Thus, the as-deposit films are mainly composed of amorphous phases with low crystallinity, the films annealed around the Curie point (120°C in our experiments) and the recrystallized film (annealed at 155°C) have moderate crystallinity, and the crystallinity of films annealed at 140°C is the best.

The ferroelectric switching current responses recorded by a homemade Sawyer-Tower circuit are demonstrated in Fig. 2, in which the ordinate represents the switching current response induced by a triangular voltage (as scaled by the abscissas). A much larger current response and a much sharper switching peak (as shown in Fig. 2) were obtained as the annealing temperature increased to 140°C. However, when the films were annealed higher than the melting point (at 155°C), they were recrystallized and showed a small current response and a wide switching peak. This result is well in accordance with that of the XRD analysis, in other words, the sharpness of the switching peaks can also be regarded as an indicator of crystallinity. Besides, much larger leakage current could be found in the as-deposit films and the films annealed at 155°C, as shown in the insert of Fig. 2. The leakage current was changed almost linearly with the applied driving voltage, and the slope of leakage current curve of the as-deposit films was slightly larger than that of the films annealed at 155°C. The occurrence of leakage current implies that there are much more structural defects in the low-crystallized films. That is, the process of crystallization may remedy the defects of films.

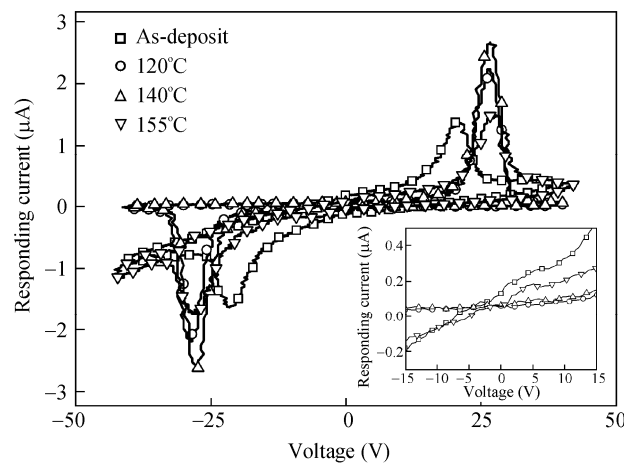


**Fig. 2** Switching current response obtained from copolymer films after different annealing treatments. Insert is a detailed image of the leakage current.

The degradation of polarization-voltage ( $P$ - $V$ ) hysteresis loops with the increase of repeated polarization switching is recorded in Fig. 3. For the films annealed at 140°C with high crystallinity, the virgin  $P$ - $V$  loop in Fig. 3(a) demonstrated a nearly rectangular shape and had the highest  $P_r$  (remanent polarization). As the cycles of polarization switching increased, the  $P_r$  value gradually reduced. The films annealed at 120°C had the similar situation. For the as-deposit films with low crystallinity, the virgin loop in Fig. 3(b) displayed a rounded shape,

while that of the melted films (annealed at 155°C, in Fig. 3c) showed a shape between rectangular and rounded ones. The fatigue process of these melted films was close to that of films with high crystallinity in Fig. 3(a).

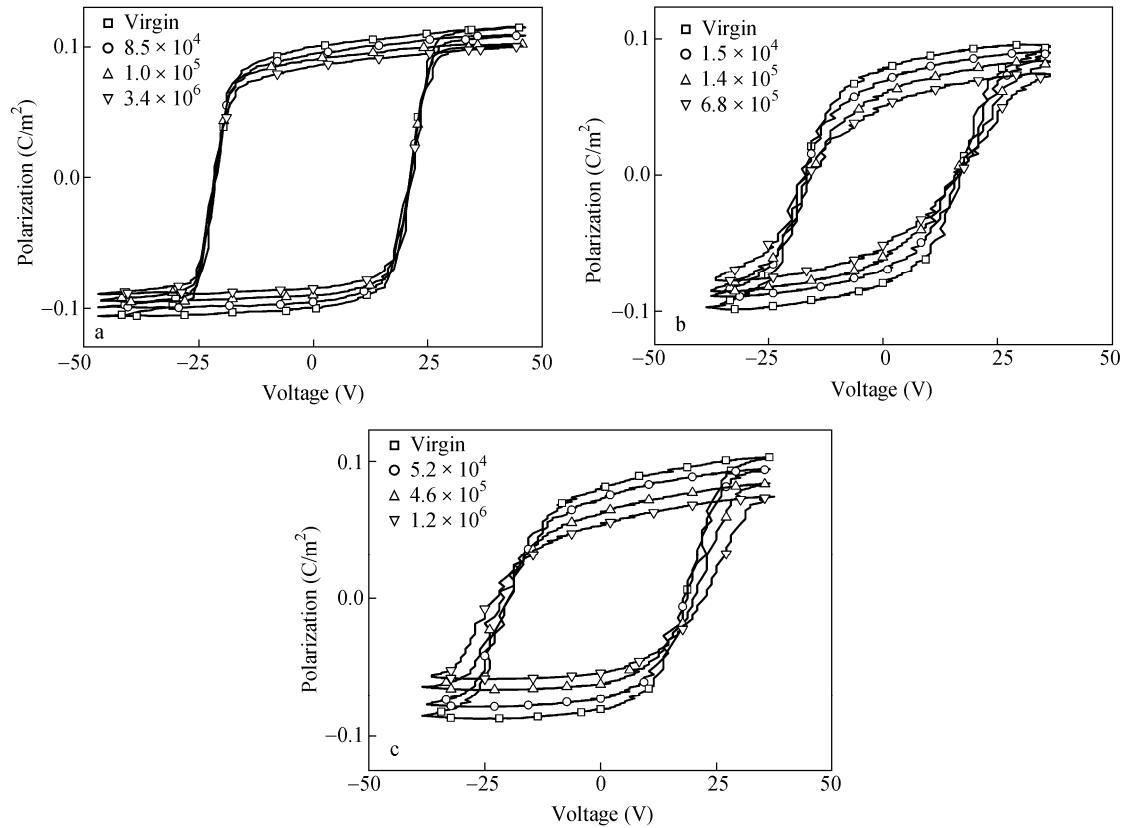


**Fig. 3** Hysteresis loops of P(VDF-TrFE) films annealed at 140°C (a), the as-deposit films (b) and films annealed at 155°C (c)

Fatigue was caused by a bipolar triangular voltage with amplitude of 40 V and frequency of 100 Hz; The top-left labels in each figure indicate the corresponding number of switching cycles.

Both our previous work<sup>[15]</sup> and the microscopic studies of Li *et al.*<sup>[14]</sup> have proved that either in amorphous or in crystalline phases, the dipoles can be reversed under a high enough electric field. The dipoles in crystalline phase are stabilized by a quasi-hexagonal-symmetry lattice field<sup>[13]</sup>, the corresponding coercive field shows a much narrower distribution, and the  $P$ - $V$  loops display a rectangular shape (as shown in Fig. 3a). However, the dipoles in amorphous phase lie in a disordered circumstance, their surroundings are different from each other<sup>[14]</sup>, so the coercive field shows a much wider distribution, and the  $P$ - $V$  loops display a rounded shape (as shown in Fig. 3b and Fig. 3c).

The comparison of fatigue rate is clearly illustrated by the relationship between the number of switching cycles and the normalized remanent polarization of P(VDF-TrFE) films with different crystallinity, as shown in Fig. 4. The fatigue rate slowed down gradually as the crystallinity of P(VDF-TrFE) films was improved. For example, given the switching cycle of  $1.0 \times 10^5$ , the remanent polarization values of as-deposit films and films annealed at 120°C, 140°C and 155°C had been reduced to 78%, 86%, 95% and 90% of their virgin values, respectively. Films with the highest crystallinity (annealed at 140°C) had the best fatigue durability under our experimental conditions.

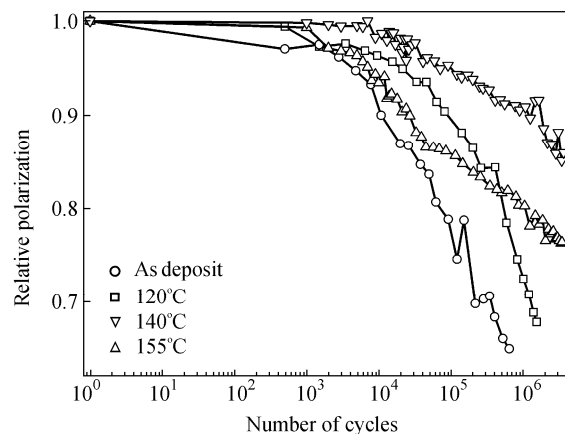


**Fig. 4** Normalized remanent polarization as a function of logarithm of the number of cycles for as-deposit films and films annealed at 120°C, 140°C and 155°C, respectively

In the studies of polarization fatigue of inorganic ferroelectrics, Pawlaczyk *et al.*<sup>[16]</sup> proposed a hypothesis that the inhibition of seeds of opposite domain nucleation, caused by the nearby-electrode injection of space charges, was the main mechanism of fatigue. In our previous work<sup>[7]</sup> we have found out that the polarization fatigue rate of copolymer films depended on the amplitude, frequency, waveform and polarity of the applied driving voltages. According to the Pawlaczyk's hypothesis, we believe that the polarization fatigue in P(VDF-TrFE) copolymer films should be attributed to the injection of charges from electrodes, and these charges can be trapped at the boundaries of crystallites<sup>[17]</sup> or captured by the defects existing both in crystalline phase and in amorphous phase of P(VDF-TrFE) copolymer films. These trapped charges may restrict the ferroelectric switching process and cause the polarization fatigue. This hypothesis should be used as well to interpret the crystallinity dependence of polarization fatigue observed in this paper.

Because the low-crystallized films (as-deposit films) have much more defects than the moderate-crystallized films (annealed at 120°C and 155°C) and the high-crystallized films (annealed at 140°C), as we mentioned above, these films may capture much more charges which inhibit the dipole rotation and have faster fatigue rate. For the moderate-crystallized films, the melted films possess lower crystallinity obtained from XRD results and induce weaker leakage current shown in Fig. 2 than films annealed at 120°C, so they may have more defects and faster fatigue rate. Similarly, because the process of crystallization may remedy the defects of films, as we mentioned above, the films annealed at 140°C have slower fatigue rate than those annealed at 120°C.

Besides the effect of defects, the morphological character may have some influence on the fatigue rate, especially in moderate-crystallized films and high-crystallized films. AFM morphologies (Fig. 5) demonstrate the change of film structure with the increase of annealing temperature. The surface of the as-deposit films (Fig. 5a) was covered by large spherical particles with diameter of *ca.* 800–1200 nm. The boundaries between adjacent particles were quite obvious. Both XRD analysis (Fig. 1) and our previous microscopic measurements<sup>[18]</sup> have proved that these particles were mainly composed of amorphous phase. After the film annealed at 120°C (Fig. 5b), a mass of fine particles with diameter of *ca.* 100–200 nm grew out of those large particles, and the boundaries between those large grains became blurry. These fine particles are primarily attributable to the crystalline phase<sup>[18]</sup>. As the annealing temperature was increased up to 140°C (Fig. 5c), these fine particles grew up to strip-like domains of *ca.* 100 nm in width and *ca.* 500 nm in length, and the crystallinity was also dramatically improved (as shown in Fig. 1). While at 155°C (Fig. 5d), films were melted and recrystallized to a mesh texture with relatively low crystallinity (as shown in Fig. 1).

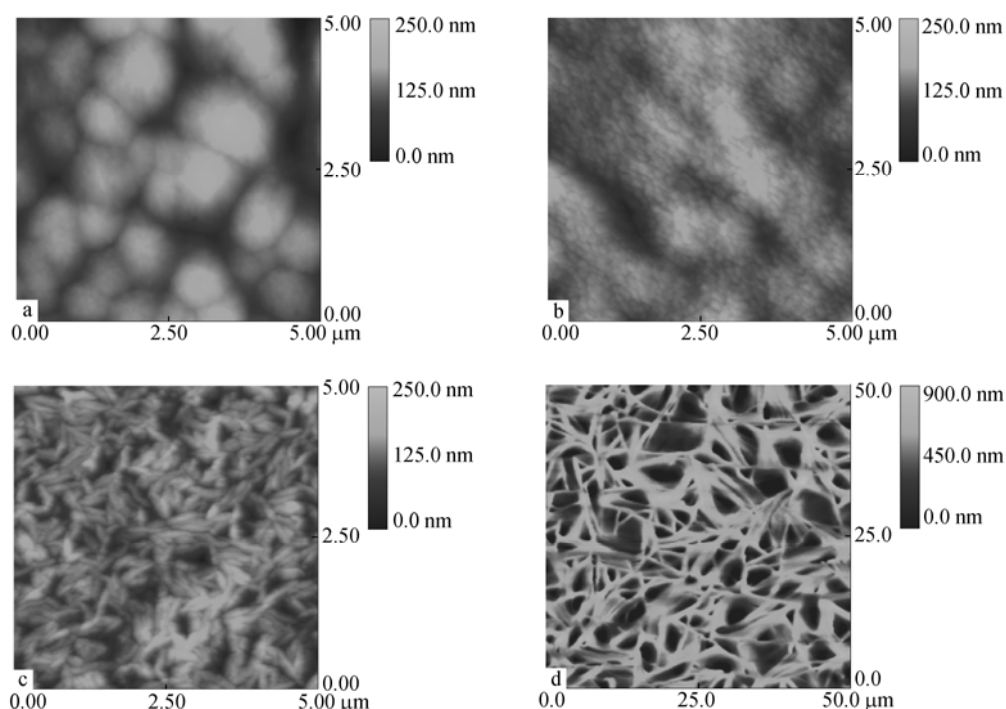


**Fig. 5** AFM morphologies of as-deposit copolymer films (a) and the films annealed at 120°C (b), 140°C (c) and 155°C (d), respectively

There is a process of particle growth when the annealing temperature rises from 120°C to 140°C, as shown in Fig. 5(b) and Fig. 5(c). Although the particles in Fig. 5 may be not equivalent to crystalline grains of P(VDF-TrFE), the change of particle shape from the films annealed at 120°C (Fig. 5b) to those annealed at 140°C (Fig. 5c) may be induced by the process of grain growth which may improve the crystallinity. Because the specific surface area of films composed of small grains could be larger than that composed of large grains, more charges may be trapped at the grain boundary and faster fatigue rate may be caused. This may be another reason that the fatigue rate of the films annealed at 120°C is faster than that of films annealed at 140°C.

Although the hypothesis of charge injection has been put forward to interpret the phenomenon of polarization fatigue in copolymer films both in this paper and in our previous work<sup>[7]</sup>, further experimental and theoretical studies are necessary to verify the conformity between experiments and theory and to deeply reveal the mechanism for the ferroelectric fatigue of the ferroelectric polymers.

## CONCLUSIONS

In conclusion, we have studied the effect of crystallinity on polarization fatigue of ferroelectric P(VDF-TrFE) copolymer films. Both XRD analysis and AFM characterization illustrated that proper annealing treatments between the Curie point and the melting point could greatly improve the degree of crystallinity of P(VDF-TrFE) copolymer films. The fatigue tests indicated that with the increase of crystallinity, a better fatigue durability and a slower fatigue rate can be obtained. The hypothesis of charge injection was introduced to explain our experimental results.

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