

Temperature Dependence of Polarization Fatigue in Ferroelectric Vinylidene Fluoride and Trifluoroethylene Copolymer Films

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ABSTRACT: In this study, we report the temperature dependence of polarization fatigue in ferroelectric copolymer films. Studies on temperature effect show a non-monotonic change of fatigue rate with increasing temperature. At temperature below $\sim 90^\circ\text{C}$, fatigue endurance is weakened at higher temperature; while, at temperature above $\sim 90^\circ\text{C}$, experimental data indicate that the higher the temperature, the lower the fatigue rate. X-ray diffraction spectra reveal

little changes of characteristic peak before and after polarization fatigue. On the basis of the hypothesis of charge-injection-induced fatigue, we propose a possible explanation of our experimental results. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3945–3949, 2008

Key words: fatigue analysis; ferroelectricity; fluoropolymers; temperature dependence

INTRODUCTION

Since the discovery of ferroelectric and piezoelectric properties in poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene [P(VDF-TrFE)],^{1,2} ferroelectric polymers have been intensively studied for their applications to transducers, sensors and actuators, and their potentials in high-density data storage.³ Recently nonvolatile memory elements, such as metal-ferroelectric-insulator-semiconductor capacitors⁴ and organic field-effect transistors,⁵ based on ferroelectric polymer films have been realized.

Polarization fatigue (the reduction in switchable polarization of ferroelectric thin films due to electrical stress) is a serious factor which has restricted the applications of ferroelectrics in nonvolatile memory devices. A large number of experiments have been carried out on fatigue in inorganic ferroelectrics and several models have been proposed.⁶ However, seldom attention has been focused on polarization fatigue of ferroelectric polymers. In our previous work,⁷ we have given a basic description of fatigue in P(VDF-TrFE) copolymer films and have found that fatigue rate is dependent on frequency, amplitude, waveform, and profile of applied fatigue voltage. Temperature dependence of polarization fatigue is also a crucial factor which may restrict the application range of memory devices, however, no studies

have been performed in this field. In this article, we will report the temperature dependence of polarization fatigue in P(VDF-TrFE) copolymer films.

EXPERIMENTAL METHODS

Copolymer films were prepared by spin-coating method from a 5.0% by weight solution of 78/22 random P(VDF-TrFE) in butanone. The films had a thickness of ~ 600 nm measured by Surfcoater ET 3000 (Kosaka Laboratory, Japan). Films were annealed at 140°C for 6 h to increase their crystallinity. The topography of these films before and after annealing treatment was characterized by a scanning probe microscope (Veeco, Nanoscope IIIa). Both top and bottom Al electrodes (about 30 nm thick) were vacuum deposited. More details on the preparation of this sandwich structure were reported in Ref. 8. Films were placed into a thermostat with a given temperature to study the influence of temperature on polarization fatigue.

Measurements of ferroelectric property were performed by a homemade sawyer-Tower circuit. Hysteresis loops were obtained by integrating the current response during ferroelectric switching process. The films were fatigued by applying an alternating triangular switching voltage with amplitude of 60 V, high enough to cause ferroelectric switching, and frequency of 100 Hz. The fatigue process was interrupted at precalculated intervals to monitor the hysteresis loop by a triangular voltage with the same amplitude and at a frequency of 1 Hz.

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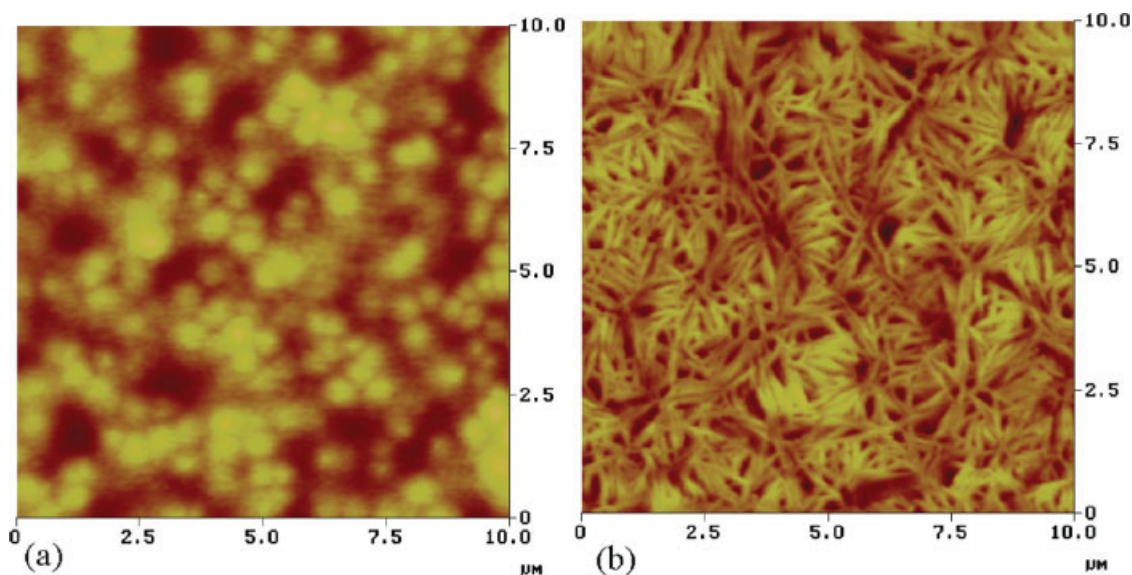


Figure 1 SPM topography of P(VDF/TrFE) films before (a) and after (b) annealing treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

X-ray analyses of copolymer films before and after polarization fatigue were performed by D8 Advance (Bruker, Germany). First, X-ray diffraction data were obtained from the poled but un-fatigued sample, and then the sample was fatigued at room temperature until its remanent polarization (P_r) decreased to 50% of its initial value. Again X-ray analysis was made from this fatigued sample.

EXPERIMENTAL RESULTS

The topography of P(VDF/TrFE) films before and after annealing treatment was shown in Figure 1. The surface of as-cast films was covered with spherical grains with the diameter of 600–900 nm [Fig. 1(a)]. Force modulation study in our previous work indicated that these grains mostly consisted of amorphous phase.^{9,10} The surface of annealed and well-grown P(VDF/TrFE) films was mostly covered with rod-like domains, which formed chrysanthemum structure [Fig. 1(b)]. Our previous force modulation imaging also showed that these rod-like structures in topographical images were corresponding to crystalline phase. Proper annealing treatment could greatly modify the structure and the phase content of ferroelectric polymer films.

First, we studied the temperature dependence of ferroelectricity and determined the temperature range above which ferroelectric property of films would be lost. This result was apparent from Figure 2. At the range from room temperature to 120°C, P_r obtained from copolymer samples were nearly kept constant, and P_r measured at 120°C decreased only by ~ 5%, compared with P_r at room temperature. When the temperature was high enough to exceed

the Curie temperature of such films (~ 128°C from Ref. 11), ferroelectric property had completely vanished. So in this article the temperature range we were interested in was focused from 25 to 120°C.

Figure 3 showed the degradation of hysteresis loops (P-V loops) with the increase of repeated polarization switching. Several significant features were apparent from Figure 3. For the samples fatigued at 25°C [Fig. 3(a)], the virgin sample showed a loop with rectangular shape and had the highest P_r ; however, with increasing cycles of polarization switching, P_r was gradually reduced accompanied by a tilt of the loop body, the shape of loops was also strongly modified from a rectangular to a rounded shape, and the coercive field showed a much

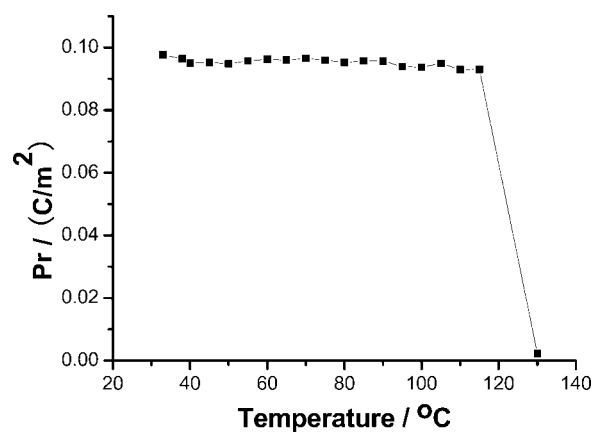


Figure 2 Remanent polarization as a function of temperature. P_r was measured by integrating the current response during ferroelectric switching process. Ferroelectric switching was excited by a bipolar triangular voltage with amplitude of 60 V and frequency of 1 Hz.

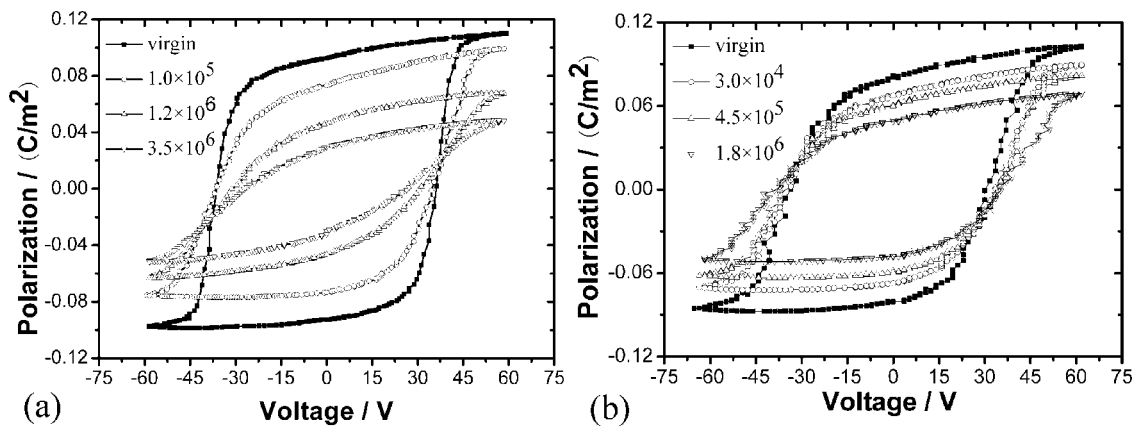


Figure 3 Hysteresis loops of P(VDF-TrFE) films obtained at the temperature of (a) 25°C and (b) 80°C. Loops were measured at the beginning and after repeated cycles of switching. Fatigue was carried out by a bipolar triangular voltage with amplitude of 60 V and frequency of 100 Hz. The labels in figure indicated the corresponding number of switching cycles.

wider distribution. For the samples fatigued at 80°C [Fig. 3(b)], the virgin sample showed a more rounded loop than that of samples fatigued at 25°C. The fatigue process was the same as that of samples at 25°C.

To determine the effect of temperature on polarization fatigue, a series of samples were fatigued at different temperature (30–110°C). The temperature dependence of normalized P_r was shown in Figure 4. Experimental data showed a very interesting result. When the temperature was below $\sim 90^\circ\text{C}$ [Fig. 4(a)], fatigue endurance was significantly weakened with increasing temperature. For example, to reduce P_r to 80% of its initial value, it needed 4.4×10^5 cycles at 30°C, 7.3×10^4 cycles at 70°C, while it only needed 8.5×10^3 cycles at 90°C. However, when the temperature was above 90°C, the result indicated that the higher the temperature, the lower the fatigue rate, as could be seen in Figure 4(b). Again we took the switching number, after which P_r decreased to 80% of its initial value, as an example,

at 100°C the corresponding cycling number was 1.8×10^4 , at 105°C it was 7.2×10^4 , while at 110°C, it needed 1.9×10^5 cycles. Because of the increasing conductivity with increasing temperature for our thin films, no further studies were performed at higher temperature (such as at 120°C).

X-ray diffraction analyses were performed before and after the polarization fatigue of the film (Fig. 5). The curves had been smoothed simply by adjacent averaging. Because of the influence of top Al electrode, which was not removed during X-ray diffraction analysis, large noises could be observed in Figure 5. However, a characteristic peak (indicated by arrows in Fig. 5), which was attributable to β -phase of P(VDF-TrFE) copolymer films,¹² could be obviously distinguished. The result indicated no apparent difference of the peak before and after fatigue, i.e., fatigue seemed to have little effect on the X-ray spectra. This result was consistent with that reported by Guy et al.¹³

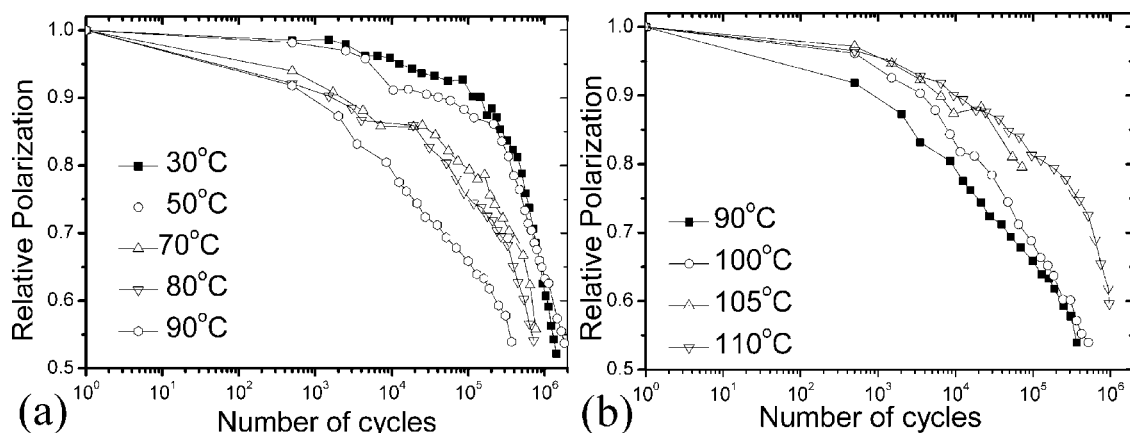


Figure 4 Normalized remanent polarization as a function of logarithm of the number of cycles. Fatigue was carried out at (a) 30, 50, 70, 80, 90°C and (b) 90, 100, 105, 110°C, respectively, and was carried out by a bipolar triangular voltage with amplitude of 60 V and frequency of 100 Hz.

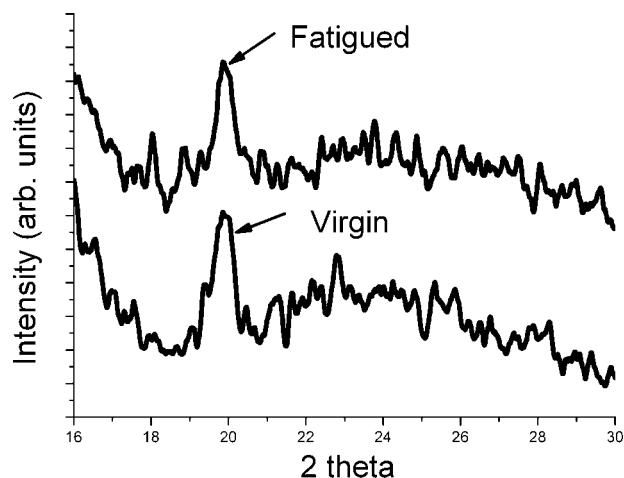


Figure 5 X-ray diffraction analyses of copolymer films before and after polarization fatigue. The plot of fatigued sample had been displayed upwards by 5 scale graduations, for clarity.

DISCUSSION

In this article, we have reported the studies on temperature dependence of polarization fatigue in P(VDF-TrFE) copolymer films. A series of experiments indicate that fatigue rate shows a non-monotonic change with increasing temperature. At temperature below $\sim 90^\circ\text{C}$, fatigue rate is enhanced with increasing temperature, while at temperature higher than $\sim 90^\circ\text{C}$, fatigue behavior is greatly improved with increasing temperature. X-ray diffraction spectra of samples before and after fatigue display no apparent difference of characteristic peak, which seems to suggest that fatigue has no influence on crystallinity¹⁴ or phase content¹² of P(VDF-TrFE) copolymer films.

To explain polarization fatigue in inorganic ferroelectrics, Pawlaxzyk et al.¹⁵ proposed a hypothesis, which suggested that the inhibition of the seeds of opposite domain nucleation, caused by the nearby-electrode injection of space charges, was the main mechanism of fatigue. On the basis of this hypothesis, we explained the frequency-, amplitude-, waveform- and profile-dependence of polarization fatigue in ferroelectric polymers.⁷ Sakai et al.¹⁶ had also reported the fatigue behavior of 75/25 P(VDF-TrFE) films and believed that fatigue originated in the pinning of negative polarization charge to the electrodes on both surfaces. X-ray diffraction analyses in Figure 5 also indicate that fatigue in ferroelectric polymers cannot be attributed to the changes of crystallinity or phase content (at least, these changes are not the major factors inducing polarization fatigue.). The possible mechanism of fatigue reported in this article is still the injection of trapped charges from electrodes into ferroelectric. These charges can be trapped at the boundary of crystallites¹⁷ and restrict the reversal of dipoles in films.

According to this hypothesis of charge injection, a possible explanation for the non-monotonic change of fatigue rate with increasing temperature, observed in this article, can be proposed. With increasing temperature, charges possess much higher energy ($k_B T$, as a factor to evaluate the contribution of thermal energy to the total energy of charges, where k_B is Boltzmann constant and T is Kelvin temperature). These charges with higher energy can penetrate from electrodes more deeply into ferroelectric, interact with dipoles in films, and finally are trapped there. This process can cause more charges trapped into ferroelectric with much faster rate, and the consequence is that the ferroelectric films are much easier to be fatigued,⁷ so this process can be called "enhanced fatigue process." In the meanwhile, higher temperature can induce another effect on polarization fatigue. The higher the temperature, the larger the energy that trapped charges possess, which make them easier to escape from the trap sites. This process decreases the density of trapped charges in ferroelectric and slows down fatigue rate, so it can be called "improved fatigue process." Obviously the enhanced and the improved fatigue processes have antithetic effects on fatigue. Whether fatigue rate is enhanced or slowed down by increasing temperature lies on which process is overwhelming. The results shown in Figure 4 seem to imply that at temperature below $\sim 90^\circ\text{C}$, enhanced fatigue process makes a major contribution to polarization fatigue, which results in the accelerated fatigue at higher temperature, while, at temperature above $\sim 90^\circ\text{C}$, improved fatigue process is overwhelming and causes lower fatigue rate at higher temperature.

The model proposed above is just a possible explanation, whose creditability should be validated by further energy calculation and molecular simulation of fatigue process in ferroelectric polymers. Perhaps structure changes of P(VDF-TrFE) copolymer at elevated temperature also make some contributions to the temperature dependence of polarization fatigue, as will be discussed in our further studies.

CONCLUSION

In conclusion, we studied the influence of temperature on polarization fatigue in ferroelectric P(VDF-TrFE) copolymer films. Experimental data showed a non-monotonic change of polarization fatigue with increasing temperature. At temperature below $\sim 90^\circ\text{C}$, fatigue rate increased with increasing temperature; while, at temperature above $\sim 90^\circ\text{C}$, the results indicated that higher temperature could improve fatigue behavior. X-ray diffraction analyses were also performed before and after polarization fatigue and implied that fatigue had little effect on crystallinity and phase content of copolymer films. On the basis of

charge-injection hypothesis, we proposed a possible explanation of our experimental results.

References

1. Kawai, H. *Jpn J Appl Phys* 1969, 8, 975.
2. Tamura, M.; Ogasawara, K.; Ono, N. *J Appl Phys* 1974, 45, 3768.
3. Matsushige, K.; Yamada, H. *Ann NY Acad Sci* 2002, 960, 1.
4. Reece, T. J.; Ducharme, S.; Sorokin, A. V.; Poulsen, M. *Appl Phys Lett* 2003, 82, 142.
5. Narayanan, U. K. N.; Bettignies, R.; Dabos-Seignon, S.; Nunzi, J. *Appl Phys Lett* 2004, 85, 1823.
6. Tagantsev, A. K.; Stolichnov, I.; Colla, E. L.; Setter, N. *J Appl Phys* 2001, 90, 1387.
7. Zhu, G. D.; Zeng, Z.; Zhang, L.; Yan, X. *Appl Phys Lett* 2006, 89, 102905.
8. Zhu, G. D.; Xu, J.; Yan, X. J.; Li, J.; Zhang, L.; Zeng, Z.; Shen, M. *Polymer* 2005, 46, 12677.
9. Zhu, G. D.; Xu, J.; Yan, X. J.; Li, J.; Zeng, Z.; Shen, M.; Zhang, L. *Thin Solid Films* 2006, 510, 181.
10. Zhu, G. D.; Li, J. *Ferroelectrics* 2004, 300, 95.
11. Koga, K.; Nakano, N.; Hattori, T.; Ohigashi, H. *J Appl Phys* 1990, 67, 965.
12. Koga, K.; Ohigashi, H. *J Appl Phys* 1986, 59, 2142.
13. Guy, I. L.; Zheng, Z.; Das-Gupta D. K. *IEEE Trans Dielectr Electr Insul* 2000, 7, 489.
14. Kepler, R. G.; Anderson, R. A.; Lagasse, R. R. *Phys Rev Lett* 1982, 48, 1274.
15. Pawlaczyk, C.; Tagantsev, A. K.; Brooks, K.; Reaney, I. M.; Klissurska, R.; Setter, N. *Integr Ferroelectr* 1995, 8, 293.
16. Sakai, S.; Date, M.; Furukawa, T. *Jpn J Appl Phys* 2002, 41, 3822.
17. Womes, M.; Bihler, E.; Eisenmenger, W. *IEEE Trans Electr Insul* 1989, 24, 461.