ELECTROSTRICTION MECHANISM IN ELECTRON-IRRADIATED FERROELECTRIC COPOLYMER:

A FREQUENCY RESPONSE MODEL

A. S. DeReggi,[1] E. Balizer,[2] D. A. Neumann[3], F. Bateman[4]

[1] Polymers Division, NIST, Gaithersburg,MD 20899-8541, USA

[2] Carderock Division., NSWC, West Bethesda, MD, USA

[3] Center for Neutron Research, NIST, Gaithersburg,MD, USA

[4]Radiation Physics Division, NIST, Gaithersburg,MD, USA

Abstract

We are investigating the physical mechanism behind the large electrostriction in the electron-irradiated copolymer of vinylidene fluoride and trifluoroethylene (mass ratio 1/1). We report on a time-resolved measurement of the thickness change that follows the application of a voltage step. This change is detected by monitoring deviations of a laser beam reflected from the electroded sample surface. We observe a prompt initial response that then decays with a relaxation time of 1 s. A model is proposed involving mobile charges that screen changes of the internal field.

Introduction

Electron beam irradiated (1 MeV, 1 MGy) copolymers of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE)] with a 1/1 VDF/TrFE mole ratio show electrostrictive strain in the thickness direction up to 4 % for an applied field of 100 MV/m [1]. It has been hypothesized that the electric field produces a reversible conversion from one crystal structure to another with a smaller lattice spacing [1]. Such transitions have been documented earlier [2-5]. Compositions with 1/1 mol or mass ratio exhibit two coexisting crystalline phases when melt crystallized [2,3] unlike compositions with much higher VDF content. One phase is analogous to the planar zig-zag (trans) conformation of the ferroelectric phase of PVDF. The other contains trans gauche (tg-tg') sequences forming a 3/1-helix as in the paraelectric phase stable above the Curie temperature of 70 °C [2,3]. Irradiation below 70 °C converts the ferroelectric phase to a phase similar to the paraelectric phase [2]. Irradiation above 70 °C stabilizes the paraelectric phase as evidenced by a lowered Curie temperature [6]. An electric field is thought to convert reversibly some of this paraelectric phase to a more compact phase presumed trans-like but not-ferroelectric.

Our recent neutron scattering results [6] established the temperature dependence of the lattice spacing and diffraction intensity of the phases present in the unirradiated and irradiated copolymer in a temperature range from −70 °C (glass transition around −40 °C) to 100 °C. These results also established limits for any field effect on the d-spacing and on the integrated intensity of the diffraction peaks for fields up to 60 MV/m, higher than the ferroelectric coercive field (50 MV/m) of the unirradiated material. These limits, in combination with the d-spacing difference between observable phases, do not support the

early attribution of the large electrostriction to solely a field-driven transformation between crystalline phases of different d-spacing.

In this paper, we report optical measurements of the time-resolved thickness change in response to applied voltage steps. We also report laser thermal pulse measurements of the residual polarization-*vs*-depth profile on voltage-poled (unirradiated) samples and on irradiated (and presumed electron-beam poled) samples. These results show kinetics affecting the transduction at low frequency that we attribute to space charge motion. We propose a simple space charge model.

Experimental

Samples: Nominally 5 cm diameter 50 μm thick films were prepared one at a time by melt-pressing pellets (approximately. 3 g per sample) sandwiched between aluminum foils using a hydraulic press with temperature-controlled platens. The thickness was set by nominally 50 μm thick steel shims placed near the corners of the platens. After pressing at 210 °C and 7 MPa for about 15 min, the foil-transported films were quenched in ambient air. Nominally 100 nm thick aluminum electrodes were applied by vacuum-evaporation.

Irradiation: Samples were irradiated in stacks of up to 10 samples in a nitrogen-flushed aluminum chamber with a 12 μm thick polyimide window. The chamber was placed in a 1 MeV electron beam exiting a van de Graaf accelerator through an aluminum window, and traveling 50 cm through atmospheric air before entering the sample chamber. Back-scattering from the bottom of the chamber contributed some secondary irradiation with an energy distribution extending below 1 MeV. Small pieces of radiation-sensitive dosimetry film were used to measure the dose absorbed by each sample in the stack. The investigated dose range was from 200 kGy to 1.4 MGy and the irradiation temperature range was from around 30 °C to around 110 °C. The doses used produced a temperature rise of up to 5 °C.

Optical measurements: Figure 1 shows schematically the electro-optical layout. A voltage is applied to a film sample inserted between a ball attached to a mirror and the flat spindle of a differential micrometer. The force maintaining the ball-spindle contact is adjustable by a spring. A thickness change of the film causes an angular displacement of the mirror about an axis defined by two other balls bonded to the mirror and riding on positioning holes in a fixed frame. Angular displacement of the mirror produces a deflection of a fine laser beam reflected by the mirror. The deflection is monitored by a two-section photodiode position-sensitive detector. The differential micrometer allows for precision in-situ calibration.

Polarization: Polarization distribution was measured by the thermal pulse method described elsewhere [7]. A nonzero thickness-averaged polarization gives a nonzero response at long times compared to the thermal transit time. The shape of the response gives the polarization distribution.

Results

Figure 2 shows illustratively the thickness change *vs* time of an irradiated sample for a sequence of applied voltage waveforms. The first voltage step produces a short rise-time response followed by a decay to zero with a relaxation time $\tau \approx 1$ s. No further response is observed when the voltage falls back to zero or when a second voltage waveform is applied. A maximum response is restored if a voltage of reversed sign is applied. These

observations indicate space charge redistribution in response to the applied field in the time scale of 1 s.

Thermal pulse measurements on unirradiated films after the application of a poling field of 60 MV/m showed the large step response expected for well poled films with uniform ferroelectric polarization. Measurements on irradiated samples, in contrast, showed two orders of magnitude smaller response indicative of a very small bimorphic polarization distribution.

Discussion

The existence of charge with either sign in the irradiated samples, in energetically shallow or deep traps, should come as no surprise in view of the high doses used. The residual internal field created by these charges has been shown to be strong enough to pole PVDF. It also drives charge motion that tends to reduce the internal field until a quasi-steady charge distribution is established. The application of a voltage long after irradiation, as in Fig. 2, momentarily disturbs the quasi-steady field distribution and results in additional charge motion tending to cancel the change in internal field. From the decay of the response in Fig. 2, we surmise a charge relaxation time of the order 1 s.

Figure 3 shows a model for the space charge effects. In the upper sketch, we show negative charges coming from the electron irradiation with compensating positive charges making the sample neutral electrically. In the lower sketch, we show a rearrangement of charge following the application of a voltage V. The charge displacement has screened the applied field. A disappearance of the electrostrictive response would be expected.

[This paper is a preliminary version pending final approval by NIST and NSWC].

References

1. Q.M. Zhang, V. Bharti, X. Zhao, "Giant electrostriction and relaxor ferroelectric behavior in electron-irradiated poly(vinylidene fluoride-trifluoroethylene," Science **280**, pp. 2101-2104 (1998).

2. A.J. Lovinger, "Polymorphic transformations in ferroelectric copolymers of VDF induced by electron irradiation," Macromolecules, **18**, p. 910, (1985).

3. G.T. Davis, T. Furukawa, A. J. Lovinger, M.G. Broadhurst, "Structural and dielectric investigation on the nature of the transition in a copolymer of VDF and TrFE (52/48 mol. %)," Macromolecules, **15**, p. 329 (1982).

4. B. Daudin, M. Dubus, J. F. Legrand, "Effects of electron irradiation and annealing on ferroelectric VDF-TrFE copolymers", J. Appl. Phys. **62**, p. 994 (1987).

5. B. Daudin, M. Dubus, F. Macchi, J. F. Legrand, "Modification of the ferroelectric properties of VDF-TrFE copoluymers induced by electron irradiation", Nucl. Instr. and Meth. in Phys. Res. **B32**, 177 (1988)

6. E. Balizer, A.S. DeReggi, F. Bateman, D.A. Neumann, "Polarization and structural transitions of irradiated VDF-TrFE copolymers," 1999 Annual Report, Conf. Electr. Insul. Diel. Phenom. pp. 104-109.

7. A.S. DeReggi, C.M. Guttman, F. Mopsik, G.T. Davis, M.G. Broadhurst, "Determination of charge or polarization distribution across polymer electrets by the thermal pulse method and Fourier analysis" Phys. Rev. Lett. **40**, pp. 413-416 (1978).
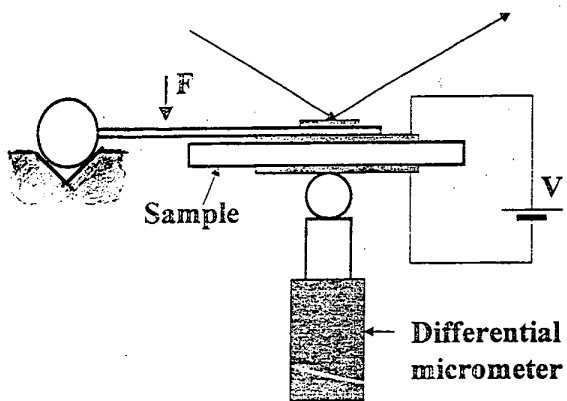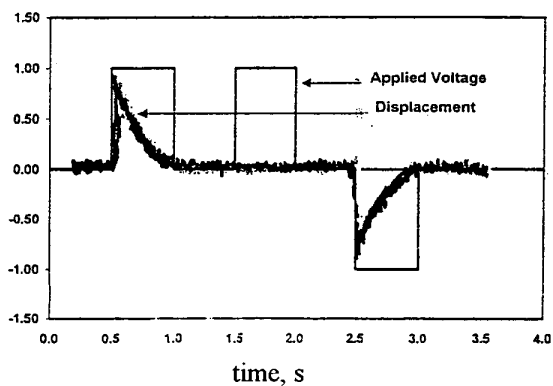
Fig. 1 Schematic.

time, s

Fig. 2 Thickness change (displacement) *vs* time
for applied voltage shown. Sample: 50 μm,
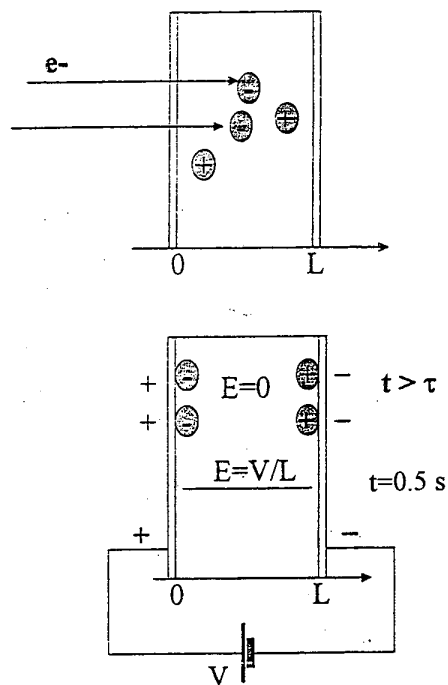1 MeV, 500 kGy, 110 °C.
Vertical scale: applied voltage, V/100;
thickness change, nm/20.

Fig. 3 Space charge model.