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Electromechanical properties of electrostrictive poly(vinylidene fluoride–trifluoroethylene) copolymer

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We report a large electrostrictive strain in electron irradiated poly(vinylidene fluoride–trifluoroethylene) copolymer at a composition with 65 mol % vinylidene fluoride, which also exhibits a large ratio of strain to applied field (~ 275 pm/V). The strain response is nearly independent of the external driving condition (unipolar or bipolar field) and does not change with temperature in about 20 °C temperature range near room temperature. Moreover, near room temperature, the material can reach a relatively high quasistatic longitudinal electromechanical coupling factor $k_{33} \sim 0.33$. © 1998 American Institute of Physics. [S0003-6951(98)03040-X]

Electroactive polymers with high electrostrictive strain and elastic energy density are very attractive for a broad range of actuator and transducer applications. Recently, we reported a massive electrostriction in electron irradiated poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)] copolymers.¹ In addition, we also showed that the new material exhibits many features resembling those of relaxor ferroelectrics, that is, the slim polarization hysteresis loop at temperatures near the dielectric peak that gradually evolves into a normal ferroelectric hysteresis loop with reduced temperature, and the dispersion of the broad dielectric peak which follows the Vogel–Folcher law.¹ The results indicate that the electron irradiation breaks up the coherent polarization domain in normal ferroelectric P(VDF–TrFE) copolymer into nanopolar regions that transforms the material into a relaxor ferroelectric. In this letter, we will present the experimental results on electromechanical properties of irradiated P(VDF–TrFE) copolymer with 65 mol % VDF.

The copolymer was from Solvay and Cie of Bruxelles. The film used in this investigation was fabricated by melt pressing powder at 225 °C and then slowly cooled down to room temperature. The film thickness was between 20 and 40 μm . The irradiation was carried out in an argon atmosphere with 3 MeV electrons and the dosage was in the range between 40 and 100 mrad. Several temperatures were chosen for the irradiation. The results reported in this letter were obtained from films irradiated at 120 °C with 60 mrad dosage. For the electric measurement, gold electrodes sputtered onto the film surfaces were used. It should be mentioned that in this investigation, we measured the field induced strain responses over a large group of specimens [both P(VDF–TrFE) 50/50 and 65/35 copolymers] under different processing and irradiation conditions, and it was found that the

specimen reported here possesses a relatively high ratio of induced strain/applied electric field among the specimens examined.

In this investigation, the electric field induced strain along the thickness direction (longitudinal strain) was characterized by a bimorph based strain sensor designed specifically for the polymer film strain measurement.² The polarization hysteresis loop was measured by a Sawyer–Tower circuit. The frequency range for the polarization and strain measurement is from 1 to 10 Hz. The elastic compliance was measured by a Dynamic Mechanical Analyzer in the frequency range from 1 to 100 Hz. Hence, the results presented correspond to the electromechanical performance of the material under nonresonance condition.

The induced strain level was examined under both bipolar and unipolar driving electric fields to compare the performance under these two different conditions. For an electrostrictive material, although in some actuator applications, it can be driven with a bipolar field, in most cases, the driving field will be unipolar. Hence, it is important for the material to have nearly the same performance under these two different driving conditions. Presented in Figs. 1(a) and 1(b) are the result obtained at room temperature. Clearly, the material exhibits a quite high strain level, -3.3% under a field of 120 MV/m with small hysteresis. Moreover, the strain levels under these two different driving conditions are nearly the same (the strain under unipolar driving is about 3% less than that under bipolar driving which is due to the existing small hysteresis). For comparison, the polarization hysteresis loop was also presented in Figs. 1(c) and 1(d). Apparently, there is only a small difference (about 5%) in the polarization level between the unipolar and bipolar driving, indicating that the small hysteresis at this temperature does not have marked effect on the polarization responses under different driving conditions. These results show that the material nearly recovers to its original zero field state after the applied field is

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FIG. 1. The field induced strains at room temperature: (a) under bipolar driving field, (b) under unipolar driving field. The polarization hysteresis loops at room temperature: (c) under bipolar driving field, (d) under unipolar driving field. The crosses in (c) is the polarization curve fit using Eq. (2) where $P_s = 0.063 \text{ C/m}^2$ and $k = 1.01 \times 10^{-8} \text{ m/V}$.

reduced to zero. Those are in sharp contrast with the behavior observed in unirradiated samples which exhibit a large polarization hysteresis and strain hysteresis.^{1,3} In addition, there is a large difference between the responses under bipolar and unipolar electric field driving conditions.

The change of the induced strain under both unipolar and bipolar driving fields with temperature is presented in Fig. 2(a), where the temperature range is limited by the current measurement setup. The data were taken under a driving field amplitude of 120 MV/m. In comparison, the polarization with temperature under the same driving field amplitude

FIG. 2. (a) The induced strain and (b) the polarization as a function of temperature (open circles are under bipolar driving field and crosses are under unipolar driving field) where the driving field is 120 MV/m. The solid and dashed curves are drawn to guide eyes.

FIG. 3. (a) The strain vs applied field at 50 °C where the strains under unipolar and bipolar driving fields are the same within the instrument resolution. (b) The polarization vs applied field where the thin curve is under bipolar field and the thick curve is under unipolar field. The two curves are nearly overlapping with each.

is presented in Fig. 2(b). Apparently, as the temperature increases, the difference in the responses between unipolar field and bipolar field approaches zero. At 50 °C, the strain versus field is nearly hysteresis free as shown in Fig. 3(a) while the polarization hysteresis is still present [Fig. 3(b)] even though the polarization curve under bipolar driving field is overlapping with that under unipolar driving field. In addition, it was found that at temperatures above 50 °C, the measured “remanent polarization” (the polarization level at $E=0$ in the hysteresis loop) increases with temperature, an indication of increased conduction in the material. As also shown in Fig. 3(b), the polarization under the unipolar driving does not come back to zero after the field is reduced to zero. All these results suggest that the hysteresis observed in the polarization responses at 50 °C and above is mainly due to the increased conduction in the material.

Clearly, the data in Fig. 2 show that between room temperature and 40 °C, under a given driving field there is only a small change of the induced strain with temperature. Above that, the reduction becomes significant. To understand what is the response for this change of strain, the electrostrictive coefficient Q_{11} was determined from the relation $S = Q_{11}P^2$ where S is the longitudinal strain and P is the polarization.⁴ The result obtained is shown in Fig. 4 and as can be seen, Q_{11} in this temperature range is nearly temperature independent and has a value of about $-12 \text{ m}^4/\text{C}^2$. Therefore, the observed reduction of the strain with temperature for a given field is a direct consequence of the reduction of the polarization. Hence, in order to achieve the same strain level, a higher field is required at temperatures above 40 °C. It should also be pointed out that the electrostrictive coefficient obtained here is much higher than those of normal ferroelectric P(VDF-TrFE) copolymers ($-12 \text{ m}^4/\text{C}^2$ compared with $-2.5 \text{ m}^4/\text{C}^2$),³ implying that the polarization

FIG. 4. (a) The electrostrictive coefficient Q_{11} (open circles) and quasistatic longitudinal electromechanical coupling factor k_{33} (filled circles) as a function of temperature under a driving field of 120 MV/m; (b) the coupling factor k_{33} as a function of the induced polarization level P_B evaluated at 23 and 50 °C based on Eq. (1) and data presented; (c) the elastic compliance as a function of temperature.

mechanism in the irradiated samples may be different from those in normal ferroelectric P(VDF-TrFE).

From the data acquired, the longitudinal electromechanical coupling factor k_{33} can be evaluated. Since the material exhibits the electrostrictive behavior, the result derived by Hom *et al.* on the quasistatic electromechanical coupling factor for electrostrictive materials is adopted here:⁵

$$k_{33}^2 = \frac{kQ_{11}^2 P_B^4}{s_{33}^P \left[P_B \ln \left(\frac{P_s + P_B}{P_s - P_B} \right) + P_s \ln [1 - (P_B/P_s)^2] \right]} \quad (1)$$

where the polarization-field (P - E) relation is assumed to follow⁵

$$|P| = P_s \tanh(k|E|) \quad (2)$$

and P_s can be regarded as the saturation polarization and k is a constant. s_{33}^P is the elastic compliance under constant polarization. Equation (1) shows that k_{33} depends on the induced polarization level P_B and hence the driving field level. For the electrostrictive P(VDF-TrFE) copolymer here, it was found that the polarization curve can be described by Eq. (2) if the average polarization is used (to eliminate the small hysteresis) as shown in Fig. 1(c) (the cross in the figure). On the other hand, if Eq. (2) is modified to include a small coercive field E_c (on the order of 5 MV/m), $|P| = P_s \tanh(k|E \pm E_c|)$, it can be used to fit the data on both branches in the polarization hysteresis loop and P_s and k are nearly the same as those determined using the averaged polarization curve. In addition, it is s_{33}^E that was measured in the experiment and Eq. (1) is modified to account for that $\{s_{33}^P = s_{33}^E [1 - (k_{33})^2]\}$.⁶ From the fit to Eq. (2), it was found that P_s in the experimental temperature range remains a constant of 0.063 C/m², and the reduction in the field induced polarization with temperature is a result of reduction of the constant k in Eq. (2). Substituting these values from Eq. (2) along with the value of P_B under a field of 120 MV/m, Q_{11} and the elastic compliance [Fig. 4(c)] into Eq. (1) yields the coupling factor k_{33} (under 120 MV/m field) as also shown in Fig. 4(a). Since the coupling factor is a function of P_B , by increasing the driving field level which raises P_B , k_{33} can be increased. As an example, the change of k_{33} with P_B is evaluated at room temperature and 50 °C and presented in Fig. 4(b). The result indicates that at room temperature, by increasing the driving field and hence raising P_B to near saturation, the quasistatic coupling factor can reach 0.33. In normal ferroelectric P(VDF-TrFE) copolymers, k_{33} is at 0.25 and even in single crystal P(VDF-TrFE) copolymer, k_{33} is still below 0.3.⁷⁻⁹ The result here demonstrates the potential of irradiated P(VDF-TrFE) copolymer in achieving relatively high electromechanical coupling factor.

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