Electron Irradiation Effects in Electrostrictive P(VDF-TrFE) Copolymers

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Abstract — Electrical field-induced strain response of electron-irradiated Poly(vinylidene fluoride - trifluoroethylene) copolymer has been studied by a Mach-Zehnder type Heterodyne interferometer in the frequency range of 3 to 9 kHz. The electrostrictive constant is calculated from the strain results, which is of the same order of magnitude as those obtained at 1 Hz by a bimorph-based strain sensor, but at much lower electrical field. Changes in the piezoelectric coefficient, dielectric property and phase transition behavior of the same copolymer have been studied. The structural changes in the irradiated films were probed by means of differential scanning calorimetry, X-ray diffraction and IR spectra. The reversible solid-state transition between the polar and non-polar phase in the crystalline regions of the copolymer driven by the external electric field is suggested to be responsible for the significant high electrostrictive strain of the electron-irradiated copolymer.

INTRODUCTION

It was found recently that the electron-irradiated Poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymers exhibit an exceptionally high electrostrictive response. Longitudinal strain over 4 % and transverse strain over 3 % were observed. The frequency range of bimorph-based strain sensor used in strain measurement is from 0.1 to 10 Hz [1-3]. Electroactive polymers with such high strain response are attractive for actuator and transducer technologies because of their mechanical flexibility, conformability, shock resistance and low acoustic impedance [4]. Depending on the application, strains at either low or high working frequency are needed for each specific application. It is significant to explore the strain response in other frequency ranges for the electron-irradiated P(VDF-TrFE) copolymers. In this paper, we present the electrostrictive coefficients of electron-irradiated P(VDF-TrFE) copolymer with 80 mol% VDF in the frequency range 3 kHz to 9 kHz. Meanwhile the structural change is investigated which will be helpful to clarify the microscopic mechanism and further improve electromechanical properties of the copolymer. All results reported here were obtained from films irradiated with 100 Mrad, for it generated the highest longitudinal strain in present study.

EXPERIMENTAL

The random copolymer of P(VDF-TrFE) used in this study, obtained from Piezotech, France, had a comonomer ratio, VDF/TrFE, of 80/20 mol.%. The raw material provided was in the form of white pellets. These pellets were dissolved in dimethylformamide (DMF) at a concentration of 20 wt.% by ultrasonic stirring for 3 hours at room temperature. Thin films were then formed by solution casting on a glass substrate, and followed by evaporation of the solvent and drying in a vacuum oven at 120°C for 24 hours. In order to increase the crystallinity of the sample, the films were isothermally treated at 135°C for 2 hours. Then, the samples were cooled to room temperature and removed from the substrate by immersion in distilled water. The electron irradiation was carried out at ambient temperature in vacuum with 3 MeV energy-level electrons. Al-electrodes were sputtered on both surfaces of the film for measurement of dielectric constant.

Strain was measured by a Mach-Zehnder type Heterodyne Interferometer [5] (SH-120 from B. M. Industries, France). The dielectric constant was evaluated by HP multi-frequency LCR meter equipped with a temperature chamber. X-ray diffraction patterns were recorded at room temperature, using CuK$_{\square}$radiation, on a Shimadzu (XD-3A) diffractometer. Differential scanning calorimeter study was performed using a PERKIN ELMER DSC7 at a heating rate of 10°C/min. To investigate the conformational changes before and after irradiation, IR spectra were recorded with the resolution of 1 cm^{-1}, using a Nicolet instrument model 170SX. Piezoelectricity measurement (d_{33}) was performed in samples polarized after irradiation (100MV/m) at 80°C for 30 min and after stabilization of polarization.

RESULTS AND DISCUSSION

Limited by the setup used, the low cutoff frequency for the strain measurement is around 3 kHz and high-end frequency is 10 kHz. Figure 1 shows the relation between the longitudinal strain and the electric field at frequency of 5 kHz. Since the copolymer films thicker than one hundred micron had to be measured in the air, the

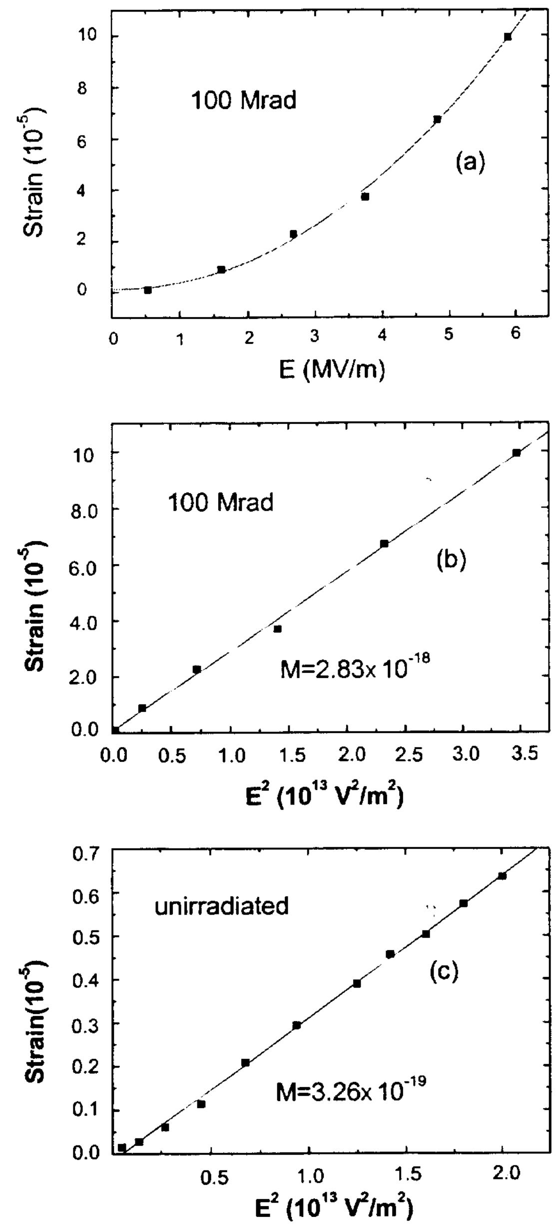


Fig. 1. The amplitude of longitudinal strain as a function of electric field. (a) quadratic function. (b)(c) linear function

maximum electric field is only 8 MV/m to avoid possible sample break down. The plot of unirradiated film is also presented in figure 1 for comparison. It can be seen from fig. 1 (a) that the strain of 100 Mrad irradiated film is a quadratic function of E due to the pure electrostrictive effect. The results were then plotted as strain vs E^2 and obtained a linear relationship as shown in Fig. 1(b) and Fig.1(c). The electrostrictive coefficient is defined as $S=ME^2$ [6]. The slope of strain verse E^2 curve gives the electrostrictive coefficient M which is 2.83×10^{-18} $\mathrm{m}^2/\mathrm{V}^2$ for irradiated film and 3.26×10^{-19} $\mathrm{m}^2/\mathrm{V}^2$ for unirradiated film. The M value of irradiated film is of the same order of magnitude as those obtained from 50/50 mol.% copolymer by a bimorph-based strain sensor [7]. Apparently, the electrostrictive coefficient is improved markedly through high-energy irradiation. Restricted by the mechanical resonance of the bimorph-based strain sensor, previously reported strain measurement was performed at very low frequency [1-3], 1 Hz or even lower. So the present result is significant in that the electron-irradiated P(VDF-TrFE) copolymer is still a very competent candidate for actuator and transducer application in the frequency range lower than 10 kHz. It is also worthy to point out that this result was obtained at a relatively lower electric field, one order of magnitude smaller than those reported previously [1-3], on thicker P(VDF-TrFE) copolymer films (over 100 μm). It is shown that the performance of irradiated P(VDF-TrFE) copolymer films is still very good when the thickness of the films increased, which is also very useful from the view point of some transducer applications. The large increase of M constant in the irradiated materials compared with that of unirradiated ones could also be attributed to the difference in the polarization responses in the two materials.

The piezoelectric d_{33} coefficient was determined from the polarization at the film surface due to a unit stress applied along the thick direction of the film. The value of d_{33} exhibited apparent variations upon irradiation. For instance, it varied from $d_{33}\approx20$ pC/N for the unirradiated sample to 11 for the sample irradiated with 100Mrad. This change is consistent with the results of decrease of the crystallinity of irradiation samples.

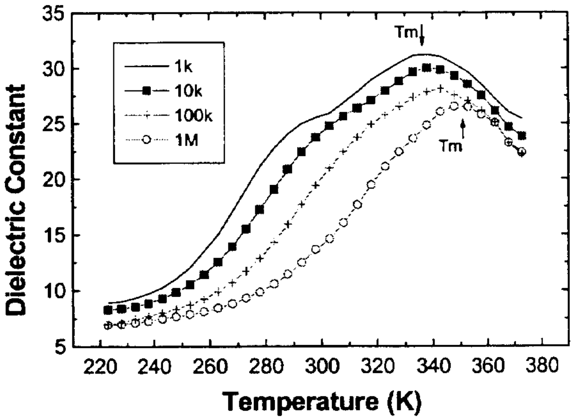


Fig. 2. The dielectric constant as a function of temperature during heating for 100 Mrad irradiated film.

The ferroelectric related properties in the electron-irradiated copolymer films were further studied by the dielectric constants measurement. The dielectric constant (ε') of irradiated film were measured as a function of the temperature for various frequency at a heating rate 2°C/min. It can be seen from figure 2 that a broad peak appears in the dielectric constant as a function of temperature. With increasing frequency, T_m (the temperature of the dielectric constant maximum) increases, while the magnitude of the peak decreases. There is no well-defined Curie' point. These experiment results demonstrated that the electron- irradiation

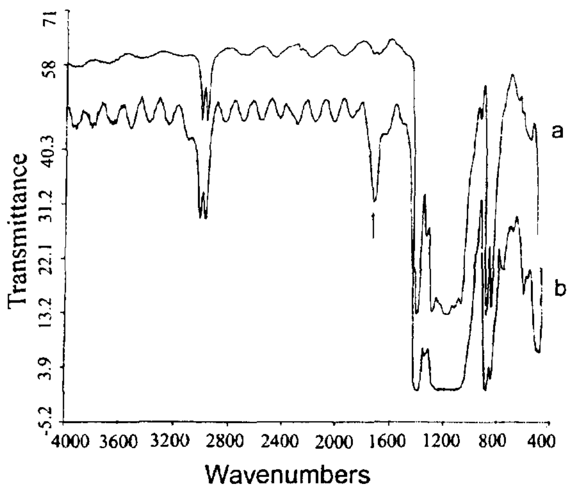
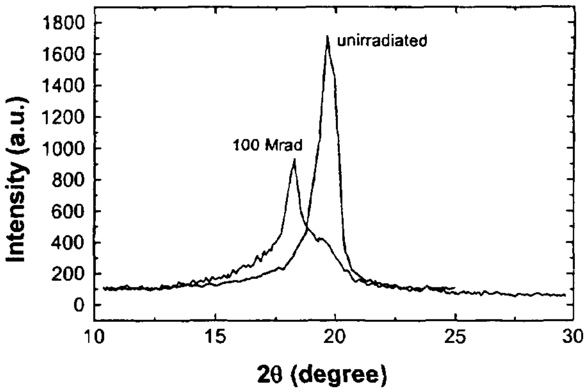


Fig. 3. Infrared spectra in the 4000-400 cm^{-1} region of P($VDF_{0.80}$-$TrFE_{0.20}$) before (a) and after (b) irradiation.



has changed the normal ferroelectric copolymer film to a ralxor ferroelectric one. From the theory of ceramics [8], It is suggested that the irradiated copolymer films contain polar regions of different size, and the distribution of both the size and polarization strength of these polar regions cause the diffuse dielectric response with frequency. It might also be the reason of the appearance of the large longitudinal strain in the irradiated film.

To clarify the electron-irradiation effect on the molecular structure of the P(VDF-TrFE) copolymer films, the infrared spectroscopic measurement were carried out. The vibration spectroscopy is very sensitive in discerning the chain configuration. The IR spectra of the copolymer films before and after irradiation are shown in Figure 3. The most prominent difference is the appearance of a sharp band at 1747 cm^{-1} in the irradiated film. This absorption peak can be assigned to a carbon-carbon double bond according to Odajima's study [9]. These microscopic defects (double bond) produced in P(VDF-TrFE) during the irradiation are basically related to dehydrofluorination reaction. That is, defects in the form of carbon-carbon double bond appear in the copolymer after the electron-irradiation.

The electromechanical activity of the copolymer mainly comes from the crystalline regions [10,11]. Therefore, the excellent electromechanical properties observed in the electron-irradiated copolymers indicate that the irradiation has a strong influence on the structure of the crystalline region. X-ray diffraction patterns of the copolymer films unirradiated and irradiated with 100 Mrad dosage are shown in Fig. 4. The X-ray diffraction peak in Fig. 5 represents Brag diffraction of (110) and (200). For the unirradiated film only a single narrow reflection at 2θ =19.7° is observed, corresponding to the polar phase. After irradiation, a broad reflection of non-polar phase centered at 2θ = 18.3° grows at the expense of the narrow reflection of polar phase at 2θ =19.7°, which become a shoulder after 100 Mrad irradiation. This means that the polar phase and non-polar phase are coexisted in the crystalline regions after irradiation. It is also noticed from the X-ray diffraction result that the full width at half maximum of the polar phase peak increased with the irradiation dosage while the integrated peak intensity decreased. This indicates the decreases of both the volume fraction of lamella crystalline phase and the average size of the polar crystalline phase in the irradiated copolymer films. The later factor is believed to be helpful to reduce the energy barrier between polar and non-polar phase in the crystalline regions of the copolymer films and facilitate the reversible solid state phase transition between these two phases driven by externally applied electric field. it is suggested that the reversible solid-state transition between polar and non-polar phases in the crystalline regions of the irradiated copolymer driven by the externally applied electrical field is responsible for the microscopic mechanism of the high strain response observed in the irradiated copolymers.

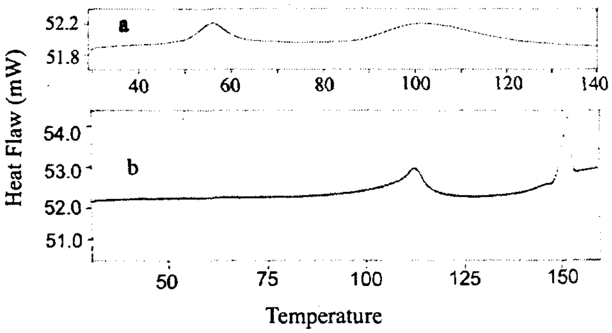


Fig. 5. Differential scanning calorimeter results of P($VDF_{0.80}$-$TrFE_{0.20}$).

Differential scanning calorimeter experiments show significant change of both the phase transition and crystallization behaviors in the copolymer films. The unirradiated sample exhibits two endothermic peaks located at 113.59 °C and 151.36 °C. The peak at low temperature is associated with phase transition between nonpolar and polar phases in the crystal regions, while the one at high temperature reflects the melting behavior nonpolar and polar phases in the crystal regions, while of the crystal regions in the materials. It is calculated that the enthalpy of two peaks decreases after irradiation, □ H_c is from 10.44J/g to 2.95J/g and □ H_m is from 14.327J/g to 7.53J/g.. In addition, the melting peak shifts to 101.2 ° and the phase transition temperature shift to 55.94 °C respectively. These results indicate that the irradiation results in the size reduction of the crystal region in the copolymer, and it is consistent with the x-ray data.

CONCLUSION

A large electrostrictive coefficient is obtained at frequency range between 3 kHz and 9 kHz in the electron-irradiated poly(vinylidene fluoride - trifluoroethyline) copolymer. Dielectric measurement shows that the material exhibits the characteristic of a relaxor ferroelectric. The influence of electron -irradiation on structure of ferroelectric copolymers has been investigated through IR spectra, X-ray, and DSC. The appearance of carbon-carbon double band has been found in irradiated copolymer from the IR spectra data. It is found that the irradiation makes both the melting temperature and phase transition temperature decrease. Based on the x-ray and DSC data, it is concluded that the degree of crystallinity and average size of polar crystal phase decreases after irradiation. It is suggested that the reversible solid-state phase transition between the polar and non-polar phases driven by the external electrical field is responsible for the excellent electromechanical properties observed in the irradiated copolymer.

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