J Mater Sci (2010) 45:6834–6836
DOI 10.1007/s10853-010-4900-y

LETTER

An electrostrictive high dielectric constant fluorinated terpolymer sheet fabricated by a melt and stretch extrusion process

Sung-Jin Kim · Ioannis Kymissis

Received: 9 July 2010 / Accepted: 4 September 2010 / Published online: 21 September 2010

Lightweight and conformable electroactive polymers (EAPs) are promising for advanced electromechanical and dielectric applications such as actuators, artificial muscle systems, and high efficiency charge storage capacitors [1–7]. EAPs are especially attractive for polymer muscle applications and demonstrate several advantages over competing approaches, exhibiting ambient operation, rapid reaction speed (microseconds to minutes), and a high mechanical energy density (~ 10 J/cm^3) [6, 8]. Polyvinilidyneflouride-trifluoroethylene (P(VDF-TrFE)) copolymers are piezoelectric and demonstrate piezoelectric properties, but are unable to achieve high strains. It has been demonstrated that by introducing defects in P(VDF-TrFE) through irradiation or introduction of a bulky non-blocking co-monomer unit such as 1,1-chlorofluoroethlene (CFE), the resulting P(VDF-TrFE-CFE) terpolymers transition into a ferroelectric relaxor and demonstrate a large electromechanical coupling and significantly reduced electrical hysteresis while retaining high dielectric constants [2, 9–11]. Recently, Bauer et al. [2] have found very large electrostrictive strains (7%) by these terpolymers.

Generally, electroactive-fluorinated terpolymers are fabricated using solution processes such as spin or drop casting followed by annealing to make crystalline thin-films with large electrostrictive coefficients [2, 9]. This process has limited ability to create uniform sheets for large area structures and high volume manufacturing. In this study, we investigate the fabrication of ferroelectric terpolymers in a favorable electrostrictive and high dielectric capacitance structure via a melt and stretch extrusion process, and demonstrate the ability of this method to produce films with favorable electrical properties, high crystallinity, and large electrostriction.

Figure 1 shows the chemical structure of the P(VDF-TrFE-CFE) and a schematic diagram of an extrusion process in which the molten terpolymer is extruded and stretched. Our fluorinated P(VDF-TrFE-CTFE) terpolymer resin was obtained from Piezotech SAS and fabricated into extruded electroactive thin-films at a constant pressure and flow rate. The extrusion process, shown in Fig. 1b, melts and extrudes the polymer using an auger. The film is extruded through a die, stretched to encourage formation of the beta phase, and rapidly quenched on a cooled roller to both rapidly solidify the film and preserve the beta phase of the material. Such an extrusion/stretch/quench process has been used to produce high-beta phase content PVDF films, and this approach appears to be effective for terpolymer compositions as well [12], enabling the production of large sheets of this material.

Figure 2 shows the electrical properties of the extruded electroactive terpolymers. The terpolymers derived from the extrusion process were sandwiched between Al (100 nm) and Al (100 nm) on glass substrates were characterized as a parallel plate capacitor with an area of 12.6×10^{-3} cm^2. Using an HP 4284A precision *LCR* meter, a capacitance density of $C_i = 2.9$ nF/cm^2 was measured, corresponding to a dielectric constant of $\varepsilon_r = 56$ at 1 kHz and ambient temperature as shown in Fig. 2a, which is comparable to that of the bulk terpolymer prepared by spin casting and Langmuir–Blodgett deposition [2, 13]. The dielectric dispersion behavior was further characterized over the frequency range from 1 to 1,000 kHz as presented in Fig. 2b. It can be seen

S.-J. Kim · I. Kymissis
Department of Electrical Engineering, Columbia University,
New York, New York 10027, USA

S.-J. Kim (✉)
College of Electrical and Computer Engineering,
Chungbuk National University, Cheongju 361-763, Korea
e-mail: ksj@cbnu.ac.kr

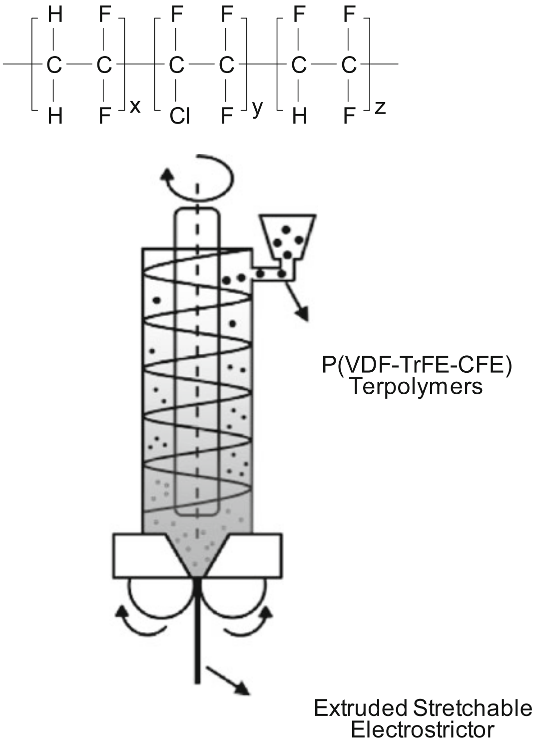

Fig. 1 Chemical structure of P(VDF-TrFE-CTE) and schematic of the extrusion process

that the dielectric constant monotonically drops from over 50 at 1 kHz to about 20 at 1,000 kHz, caused by dielectric dispersion.

The crystallinity was verified using wide-angle X-ray diffraction (XRD). The measurement was performed using a Bruker AXS X-ray diffractometer with a wavelength of 1.5406 Å in order to interrogate an interchain spacing and, through its peak width, crystalline order perpendicular to the chain direction. Figure 3 represents the XRD patterns of extruded terpolymer films. The XRD curves of the polymer before and after extrusion are shown in inset of Fig. 3: samples were denominated B* (before stretching process) and B (after stretching process), and the peak shift between B* and B can be attributed the change of β content and α crystal reorientation. The X-ray data exhibits two narrow peaks at 18.0° and 37.2° in B samples. The (110) and (200) diffractions of the films are located at $2\theta = 18.0°$, from an interchain crystal spacing of 4.9241 Å, which is consistent with the desirable β-phase for electrostrictive performance [14, 15]. This crystal lattice parameter is similar to that of other high strain terpolymer devices developed via suspension polymerization using an oxygen-activated initiator and deposited using solution processes followed by annealing [10].

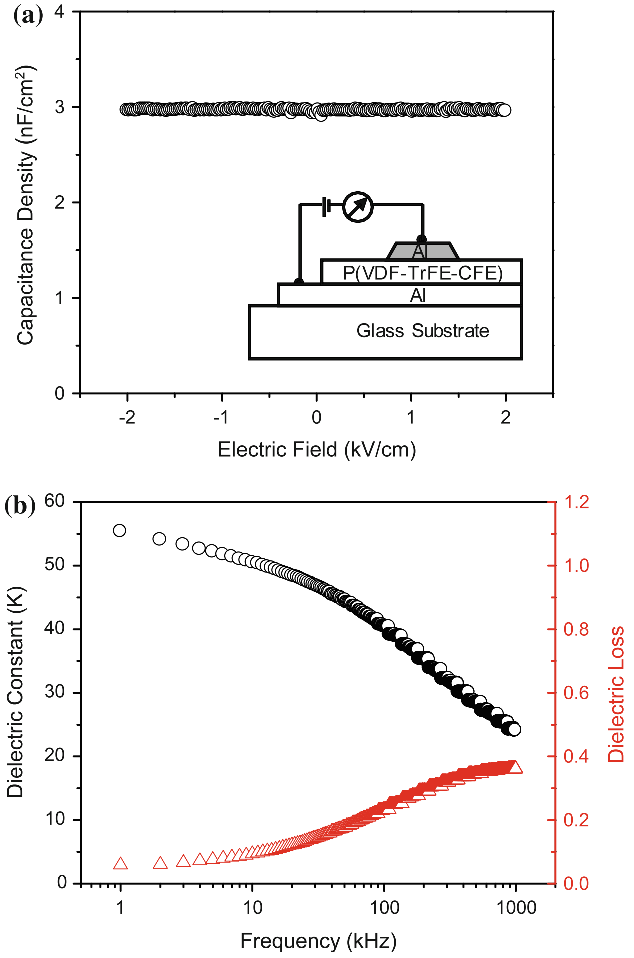

Fig. 2 **a** Capacitance density measured on a Al/extruded P(VDF-TrFE-CFE)/Al/Glass sample as a function of electric field at 1 kHz. **b** Dielectric constant of the extruded sample as a function of a frequency from 1 to 1,000 kHz at room temperature

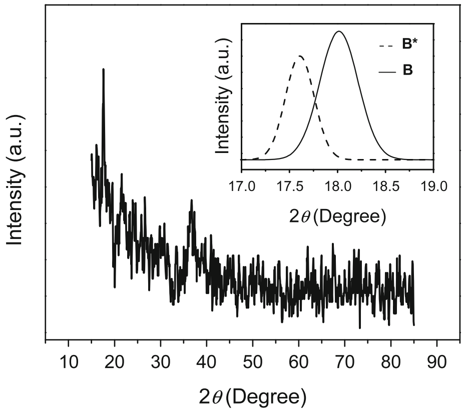

Fig. 3 Room temperature X-ray diffraction pattern of the electroactive terpolymer fabricated by the extrusion process. *Insets*: The XRD curves of the polymer before and after stretching

The terpolymer was metallized with 100 nm of aluminum, and arranged in a unimorph configuration. A field strength of 50 MV/m was applied and bending was observed and measured. The extruded films display significant bending actuation, as shown in Fig. 4. The electrostrictive nature of the thin-film terpolymer and top/

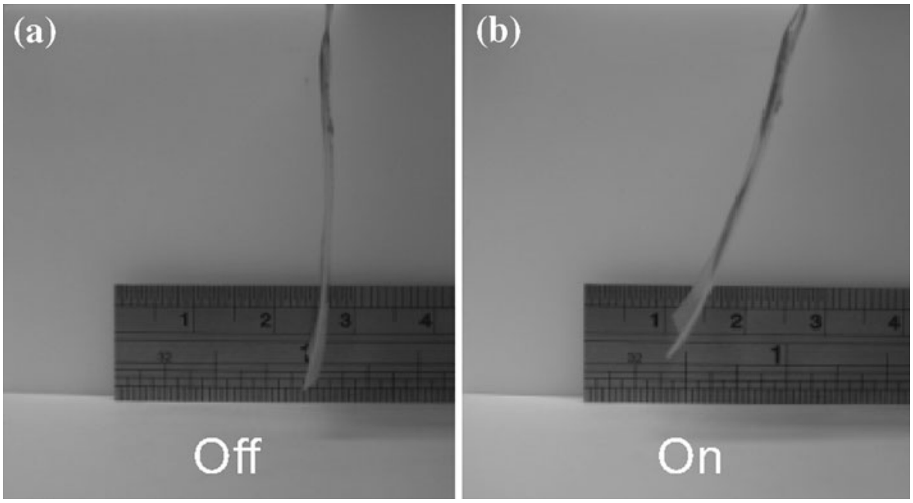

Fig. 4 Images of the bending actuation of the extruded stretchable electrostrictor. The applied field was 50 MV/m

bottom Al electrodes yields a bending actuation corresponding to 4.2% bending strain on application of electrical stimulation. This electrostrictive film, prepared through an extrusion process, presents a spontaneous response and operation in the air for long-term stability.

In summary, fluorinated P(VDF-TrFE-CFE) terpolymers have been fabricated using the extrusion process with a melt and stretch process which yields large sheets of the material with a crystallinity and crystal phase suitable for electrostrictive and capacitave energy storage applications. When metallized and structured in a unimorph, large electrostrictive behavior (>4% strain) was observed in air, allowing a high throughput alternative for polymer muscle applications.

Acknowledgements This study was partially supported by the NSF award ECCS-0644656. S-J.K. acknowledges the support of the Korean Ministry of Education, Science and Technology (The Regional Core Research Program/Chungbuk BIT Research-Oriented University Consortium).

References

1. Smela E (2003) Adv Mater 15:481
2. Bauer F, Fousson E, Zhang QM, Lee LM (2004) IEEE Trans Dielectr Electr Insul 11:293
3. Ha SM, Yuan W, Pei Q, Pelrine R, Stanford S (2006) Adv Mater 18:887
4. Shankar R, Ghosh TK, Spontak RJ (2007) Adv Mater 19:2218
5. Claude J, Lu Y, Li K, Wang Q (2008) Chem Mater 20:2078
6. O’Halloran A, O’Malley F, McHugh P (2008) J Appl Phys 104:071101
7. Li T, Chen Y, Ma J (2009) J Mater Sci 44:5393. doi:10.1007/s10853-009-3567-8
8. Neese B, Chu B, Lu S-G, Wang Y, Furman E, Zhang QM (2008) Science 321:821
9. Buckley GS, Roland CM, Casalini R, Petchsuk A, Chung TC (2002) Chem Mater 14:2590
10. Klein RJ, Runt J, Zhang QM (2003) Macromolecules 36:7220
11. Lu Y, Claude J, Neese B, Zhang Q, Wang Q (2006) J Am Chem Soc 128:8120
12. Mohammadi B, Yousefi AA, Bellah SM (2007) Polym Testing 26:42
13. Wang JL, Meng XJ, Yuan SZ et al (2008) Appl Phys Lett 93:192905
14. Kodama H, Takahashi Y, Furukawa T (1997) Ferroelectrics 203:433
15. Lovinger AJ (1983) Science 220:1115