



# Plasticized relaxor ferroelectric terpolymer: Toward giant electrostriction, high mechanical energy and low electric field actuators



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## ABSTRACT

Enhancing the electrostrictive strain under low electric field of a dielectric electroactive polymer (EAP) is essential in soft actuators applications. Conventional electrostrictive polymers suffer of the high electric fields usually required to reach sufficient strain. Here we report a new approach that greatly enhanced the strain under electric field and the mechanical energy density of fluorinated terpolymer EAP. A new all organic composite based on poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer (P(VDF-TrFE-CFE)) doped with bis(2-ethylhexyl) phthalate (DEHP) was synthesized. DEHP molecule acts as a plasticizer that leads to large dipolar interfacial effects. This chemical modification allows a 28-fold increase of the electrostrictive strain and a 215-fold increase of the mechanical energy density. As a consequence, this new approach permits the uses of the exceptional properties of the fluorinated terpolymer for an electric field nearly 5 times lower and represents a simple and effective solution to this technological barrier.

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## 1. Introduction

In a constant search for miniaturized devices such as micro-electromechanical systems (MEMS) or lab on a chip platforms, polymeric materials have been widely studied for their lightweight, low-cost and processability [1,2]. While micro-fabrication processes are now well controlled on polymers, research is now focusing on implementing “smart” polymers as actuators on these devices [3]. These polymeric materials have the ability to change dimensions upon the application of external stimuli such as heat, light or electric voltage. Electroactive polymers (EAPs) can be classified into two main categories [4]: ionic for which deformation is generated by ionic exchanges between an electrolyte and the polymer when an electric potential difference is applied to the polymer and dielectric polymers for which strain is due to the electric field generated between two electrodes. While ionic polymers are interesting in media where solvent and ionic species are available, dielectric polymers can be implemented in any kind of environment and the response time to electrical stimuli is faster. Here, we will be only focusing on the latter kind.

Dielectric EAPs are polymers showing large strain response to an electric field, making them good candidates as low frequency

active actuators. Different types of dielectric EAPs exist. Dielectric elastomers such as silicones and acrylates have been studied and strains over 100% have been recorded for very high electric field ( $>150 \text{ V}/\mu\text{m}$ ) [5]. Polyurethanes are also polymers of interest [6,7]. They are semi-crystalline and therefore show large electrostrictive effects. However, according to their low modulus of elasticity, the two kinds of polymer described above did not show large conversion of electrical energy into mechanical energy. Therefore, they are not considered useful for practical applications. Attempts to improve the strain and energy generated by dielectric EAPs mainly include the use of additives in the active polymer matrix. High permittivity ceramics and carbon have been used, showing an increase of the strain [8–11]. However, improvements were not significant and mechanical energy remained low.

More recently, Xia et al. developed a new kind of electrostrictive polymers known as fluorinated terpolymers P(VDF-TrFE-CFE)[12]. This is a semi-crystalline polymer which shows the highest level of conversion from electrical to mechanical energy. However, large electrical field are required ( $E > 100 \text{ V}/\mu\text{m}$ ) to reach sufficient strain levels ( $>2\%$ ). The main drawback of electrostrictive polymer and dielectric elastomer actuators is their high electric field requirement. High electric fields can be achieved at low voltages if the films are thin. However, since it is difficult to produce very thin films uniformly in large areas, such devices used are usually in the tens of micrometers range, requiring driving voltages in the 1 kV range. The electromechanical transduction properties of any electrostrictive

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polymers are intrinsically regulated by the dielectric permittivity of the material [14]. This parameter directly controls both the achievable active stress and strain. In order to increase the dielectric permittivity of polymer materials, different methods have been developed. The main approach is based on the dispersion into the polymer matrix of a filler, either solid (e.g. powder) or liquid [13,15–17]. However, one of the typical drawbacks of the composite approach lies in a substantial decrease of the material dielectric strength ( $E_{break}$ ). More generally, it is straightforward to recognize that higher values of the dielectric permittivity typically correspond to a lower value of dielectric strength [11,18]. In 2002, Zhang et al. proposed to add organo-metallic compounds in a fluorinated terpolymer to increase its strain at low electric fields [13]. Nevertheless, the dielectric strength in this case dropped from 200 V/ $\mu\text{m}$  for a neat P(VDF-TrFE-CFE) to 13 V/ $\mu\text{m}$  for the modified polymer, which decreased the operating range of the material, since dielectric strength decreased by 15-fold. It is therefore essential to keep the dielectric strength as high as possible for real application. Indeed, in typical actuator designs, the maximum electric field chosen is  $E_{break}/2$  for safety reason [19]. If the decrease of dielectric strength observed in composite system is too large, the operating range become smaller and, thus, the relative increase of the actuation performance in composite is not proved. Hence it is very important to develop materials able to support large electric field and high electromechanical strain to demonstrate the potential of electrostrictive polymer as artificial muscle. Although the results presented by Zhang et al. were significant, no applications arose from this material. It is potentially due to the cost of the organo-metallic complex used in the composites and the important decrease of the dielectric breakdown electric field.

In this work, fluorinated terpolymer P(VDF-TrFE-CFE) has been used. This material has gained increasing interest over the past years due to its relaxor ferroelectric behavior, high dielectric permittivity ( $\epsilon \sim 50$ ) and high electrostrictive strain [20]. The high dielectric permittivity of this polymer comes from the cooperative dipole orientation within the crystalline phase of the polymer which leads to a relaxor ferroelectric material. The high mechanical energy density compared to others electrostrictive polymers make this material suitable in industrial applications such a varifocal lens [21–23]. In this study, fluorinated terpolymer has been doped with bis(2-ethylhexyl) phthalate (DEHP). This modified terpolymer shows a 28-fold increase of the electrostrictive strain under low applied electric field and a 233-fold increase in mechanical energy compared to the unmodified polymer. This simple chemical modification allows the use of the exceptional properties of the terpolymer at an electric field 5.5 times lower than that of the neat terpolymer. In addition, the modifications we proposed here is cheap, simple and could potentially break a technological lock.

## 2. Materials and methods

### 2.1. Sample elaboration

The P(VDF-TrFE-CFE) 56.2%/36.3%/7.5% terpolymer powder was purchased from Piezotech S.A.S (Arkema group). Films were made from solution cast. In a first step P(VDF-TrFE-CFE) was dissolved in Methyl Ethyl Ketone (MEK, Sigma–Aldrich) with a polymer to MEK mass fraction of 14%. Then, the solution was cooled at room temperature for 2 h. In a second step, (2-ethylhexyl) phthalate (DEHP, Sigma–Aldrich) was added and stirred for 1 h. Finally, the mixture was cast onto a glass substrate using a Doctor blade (Elcometer) and the solvent allowed to evaporate. The films were placed in an oven at 60 °C for 12 h to totally remove the solvent followed by and annealing at 103 °C for 1 h to improve the crystallinity of the samples. The thickness of the as-prepared films was 50  $\mu\text{m}$ . For

electrical measurements, 25 nm gold electrodes were sputtered on each side of the sample using a Cressington Sputter Coater (208 HR).

### 2.2. Differential scanning calorimetric characterization

Differential scanning calorimetric measurements of the different polymers were performed on a DSC 131 EVO calorimeter from Seteram Instrumentation. The samples were heated up to 160 °C for 5 min. The samples were cooled to room temperature (cooling rate 10 °C/min), and kept at room temperature for 5 min. Then, the samples were heated to 160 °C with a heating rate of 10 °C/min and the measurement recorded. This procedure was performed twice to confirm the reproducibility of the measurement.

### 2.3. Mechanical properties

A 4 cm length, 1 cm width and 50  $\mu\text{m}$  thick sample was clamp on one side on a fixed clamp and on the other side to a mobile clamp. A Newport table microcontroller and a force sensor were used to measure the displacement and the force, respectively, and convert in strain and stress of the sample. The displacement speed was 0.3 mm/s. The Young modulus of the samples was determined by the slope of the linear dependence of the stress versus strain.

### 2.4. Longitudinal strain under electric field measurements and electrical characterization

Fig. 1 shows the dedicated test bench realized to measure the strain versus electric field in compression. The strain was measured with the help of a non-contact capacitive measurement sensor (FOGALE MC 940) with a precision on the order of 10 nm. Because P(VDF-TrFE-CFE) were elastically much softer than ceramics and the samples were made into very thin films, great care must be taken in the strain measurements of P(VDF-TrFE-CFE) to ensure the accuracy of the data when applied an electric field on it. For such soft film flexure motion and mechanical clamping of a sample are two major causes of errors in the strain measurements. The film samples were placed on horizontal stainless steel disks (20 mm in diameter) in order to avoid measuring a parasitic flexure motion, and a second brass disk positioned on the top of the film rendered it possible to apply a bipolar electric field. The total weight of pieces 3, 4 and 5 shown in Fig. 1 was 5 g (equivalent to 156 Pa) which was a suitable small stress, in order to avoid clamping of the sample. The sample was subjected to electric field with the help of a waveform generator (Agilent 33220A) for which the output was amplified through a high voltage amplifier (model 10/10, Trek Inc.), the displacement and voltage were monitored with the help of an oscilloscope (Agilent – DSO7034A). The strain was deduced by divided the displacement by the initial thickness. At the same time, the current was monitored using a current amplifier Standford SR-570 and polarization has been calculated.

## 3. Enhancement of the electrostrictive response of dielectric EAP

It has been previously shown that in the case of dielectric polymers, the electrostrictive strain under electric field can be mainly attributed to Maxwell forces induced by dipolar orientation within the material [14]. In the longitudinal direction, the compressive Maxwell strain and the mechanical energy density under electric field are given by Eqs. (1) and (2):

$$S_{33} = -\frac{\epsilon\epsilon_0}{2V}(1 + 2\nu)E^2 \quad (1)$$

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