

Recent Advances in highly Electrostrictive P(VDF-TrFE-CFE) Terpolymers

F. Bauer*, E. Fousson

Institut Franco-Allemand de Recherches de Saint-Louis
68300 Saint-Louis, France

Q. M. Zhang

Electrical Engineering Department and Materials Research Institute
The Pennsylvania State University
State College, PA 16802, USA

ABSTRACT

Ferroelectric materials are intrinsically multifunctional and have found a broad range of applications. A new class of semicrystalline terpolymers comprising vinylidene fluoride (VDF), trifluoroethylene (TrFE), and 1, 1-chlorofluoroethylene (CFE), were prepared at ISL via a suspension polymerization process. Relevant studies and results show that this class of electroactive polymers offers unique properties in comparison with other ferroelectric polymers. The terpolymer exhibits high electrostrictive strain ($>7\%$) with relatively high modulus ($>0.3\text{GPa}$). It has been also observed that the large electrostrictive strain is nearly constant in the temperature range from $20\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$. The high room temperature relative dielectric constant (~ 50), which is the highest among all the known polymers, high induced polarization ($\sim 0.05\text{ C/m}^2$), and high electric breakdown field ($>400\text{ MV/m}$) lead to very high volume efficiency for the electric energy storage operated under high voltage ($\sim 10\text{ J/cm}^3$).

Index Terms — Electrostrictive polymer, actuators, capacitors.

1 INTRODUCTION

Ferroelectric materials like Poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene P(VDF-TrFE) are intrinsically multifunctional. In the copolymer with TrFE these ferroelectric polymers will exhibit a Curie transition, where a phase transition between the ferroelectric and paraelectric phases occurs with increasing temperature. In the poled ferroelectric phase, these polymers exhibit relatively high piezoelectric response and have found a broad range of applications [1, 2]. However, the low responses in the traditional ferroelectric materials such as low strain level ($\sim 0.1\%$ strain) and low sensitivity to external stimulus limit the performance of the devices and systems. As has been observed in many ferroelectric materials, by operating near the instability regions such as ferroelectric-paraelectric (F-P) transitions, many of these responses can be significantly enhanced [3]. On the other hand, phase transition occurs over a narrow temperature range and, in most cases, involves large hysteresis which prevents these enhanced responses from practical and general applications. It has been found that by introducing defects into the P(VDF-TrFE) copolymers, it is possible to convert the polymer from a normal ferroelectric to a relaxor ferroelectric [4]. A new class of ferroelectric polymers, i.e., the terpolymers of P(VDF-TrFE-CFE), was developed from the normal ferroelectric PVDF polymer by employing proper defect modifications which eliminate

detrimental effects associated with a normal first order F-P transition while maintaining high material responses [5-7]. The introduction of the third monomer into the polymer chain serves to interrupt the ferroelectric domains, thereby reducing their size [7]. Random defect introduction, as in the irradiated copolymer samples [3], broadens the ferroelectric transition and reduces the ferroelectric-paraelectric transition temperature. The random incorporation of the bulky third monomer into the polymer chains forces a conformation change from the all-trans ($T_m \geq 4$) or conformation to the transgauche (TG) and T_3G conformations [8,9].

The figure 1 shows the molecular conformations for PVDF

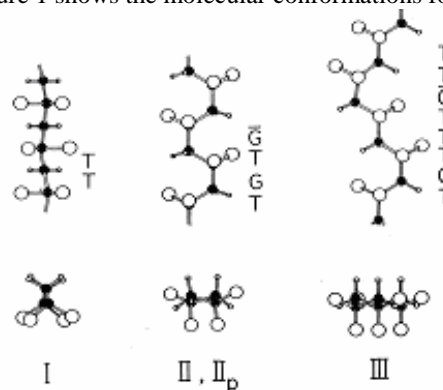


Figure 1. The conformations of the different phases of PVDF.

based polymers [10]. Addition of defects in the form of chemical monomers, in this case 1, 1-chlorofluoroethylene (CFE) which are copolymerised with the VDF-TrFE, eventually favor the TG conformation and eliminate the normal ferroelectric phase, leading to a relaxor ferroelectric with electromechanical strain greater than 7% and an elastic energy density of 0.7 J/cm^3 at 150 MV/m [11]. It is the change in conformation from the disordered TG and T_3G to the all trans conformation that leads to the observed large electrostrictive strain. This high electrostrictive strain coupled with relatively high modulus ($>0.3 \text{ GPa}$) makes the polymers suitable as a structure component in addition to the electroactive functions (actuators and sensors). This relaxor-ferroelectric terpolymer P(VDF-TrFE-CFE) exhibits a room temperature dielectric constant greater than 50 [5,7]. To our knowledge, these values are among the highest ones reported in the literature [12]. It should be borne in mind that the amount of CFE added to the P(VDF-TrFE) strongly affects the strain response and the polarization hysteresis by changing the spontaneous polarization, the crystallinity, the Young's modulus, the dielectric properties, and the structural conformations [8].

In this paper, we will present the relaxor properties as well as the capacity of these terpolymers for the storage of electric energy leading to new potential applications.

2 EXPERIMENTAL AND RESULTS

2.1 TERPOLYMER SYNTHESIS AND SAMPLE PREPARATION

The synthesis of these relaxor ferroelectric polymers at different compositions [5] has been carried out at the Institut Franco-Allemand de Recherches de Saint-Louis (ISL), France.

The terpolymers were prepared by a combination of the suspension polymerization process and an oxygen-activated initiator at a temperature of 40°C . The bulk polymerization took place at this temperature for 8 hours. The resulting terpolymer ($\sim 1.5 \text{ kg}$) was recovered, washed with distilled water and dried. This chemistry produces high terpolymers that have uniform molecular structure and few impurities. The polymers were then dissolved in methylethylketone and cast as $\sim 20 \mu\text{m}$ films. At Penn State, the polymers were then dissolved in *N,N*-dimethylformamide. Thin films were formed by pouring the solution on glass substrate and then evaporating the solvent. These films were annealed at 120°C for at least 14 hours to further remove solvent and increase the crystallinity. For electrical characterization, gold electrodes were sputtered on the surfaces. Polarization hysteresis measurements were made with the ISL circuit, and the electromechanical strain was monitored by a photonic sensor [7]. The dielectric properties were measured in a temperature chamber by an impedance meter, model HP 4284.

2.2 POLARIZATION RESPONSE

Addition of defects in the form of chemical monomers, eventually eliminates the ferroelectric phase at room temperature and moves the dielectric constant peak to room temperature. It has been shown [5-7] that by copolymerization of chlorofluoroethylene (CFE) with the

P(VDF-TrFE), the polymer can be converted to a relaxor ferroelectric which eliminated the polarization hysteresis (dielectric heating) at room temperature associated with the change of polarization, Figure 2 [8].

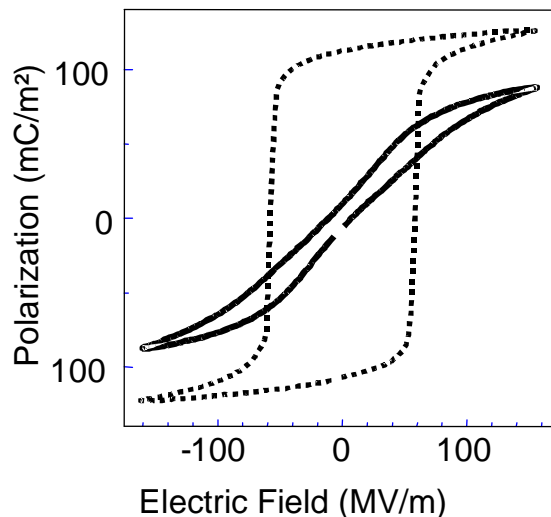


Figure 2. Comparison of the polarization hysteresis of the normal ferroelectric polymer (dashed curve, large hysteresis) and relaxor ferroelectric polymer (black curve) at room temperature.

2.3 ELECTROSTRICTIVE TERPOLYMER PROPERTIES

A unique feature of this relaxor ferroelectric polymer is the large electrostrictive strain which can be induced by external electric field [7,8,11]. An example of the thickness strain as a function of electric field is shown in Figure 3(a) for a 65/35/8.6 VDF/TrFE/CFE sample. This is a typical thickness strain plot, which shows both the quadratic dependence of strain at low electric fields and the saturation in strain as the polarization approaches saturation at high fields. The electrostrictive strain reaches more than -7% along the thickness direction. For unstretched films, the transverse strain is 3% and for the uniaxially stretched films, the strain along the stretching direction is 5% under $150 \text{ V}/\mu\text{m}$, Figure 3(b).

One objective of studying this class of terpolymer is to maximize the electromechanical properties as a function of VDF and CFE contents. Other compositions have been synthesized. Decreasing the CFE fraction below $\sim 8\%$ causes an undesirable rise in the fraction of normal ferroelectric phase in the crystalline regions, while increasing the CFE fraction above $\sim 9\%$ significantly decreases the crystallinity and the Young's modulus [8,11,13]. The electrostrictive strain for the P(VDF-TrFE-CFE) terpolymers has been found to be a maximum near 8.5% CFE, for the VDF-TrFE composition near 65/35. For these terpolymers, the observed range of the Young's modulus for unstretched samples is equal to a value ranging from $150 \text{ up to } 450 \text{ MPa}$, depending of the CFE content [8,13].

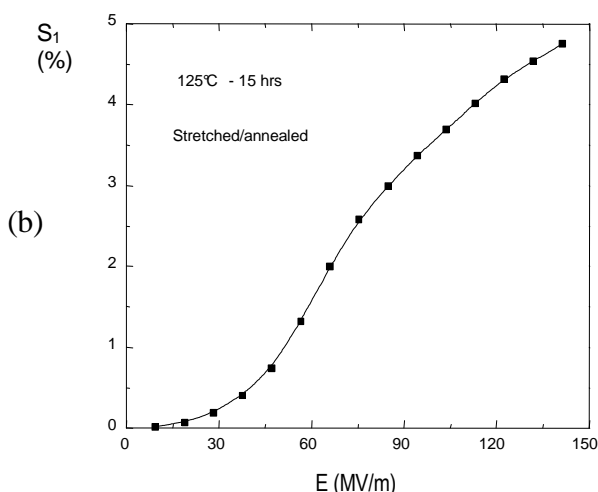
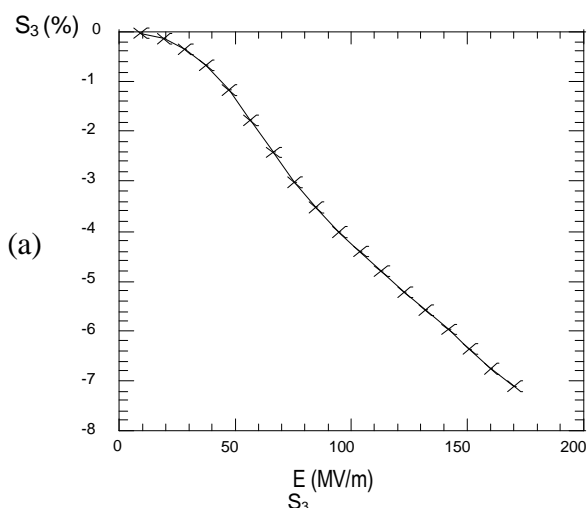


Figure 3. The electrostrictive strain of a relaxor ferroelectric polymer (P(VDF-TrFE-CFE) terpolymer): (a) Longitudinal strain, (b) transverse strains measured from stretched terpolymer films.

In the study of the electromechanical response of the relaxor ferroelectric polymers, it has been observed that the large electrostrictive strain is nearly constant in the temperature range from 20°C to 80°C, Figure 4 [11].

In Table 1 we summarize and compare the electromechanical properties of four different types of ferroelectric materials [4,6,14,15]. S_M is the maximum strain and $YS_M^2/2$ is the volumetric elastic energy density. Y is the elastic modulus along the actuation direction.

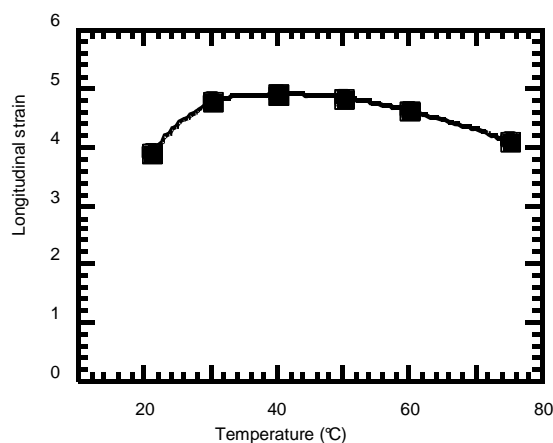


Figure 4. The electrostrictive strain as a function of temperature under 150 MV/m field.

Table 1.

Materials	Strain	Y (GPa)	S_M (%)	Stress (MPa)	$YS_M^2/2$ (J/cm ³)	$YS_M^2/2f$ (J/kg)	Coupling factor
Piezo-Ceramics (PZT-5)	S_3	54	<0.2	108	0.11	14.3	0.75
	S_1	61	<0.1	61	0.06	7.8	0.39
PZN-PT Single crystal	S_3	8	1.7	136	1.04	136	0.93
Irradiated P(VDF-TrFE)	S_3	0.5	-5.0	25	0.625	337.8	0.3
	S_1	1.0	4.5	43	1.0	500.0	0.65
P(VDF-TrFE-CFE) terpolymer	S_3	0.3	-7	21	0.73	365	
	S_1	0.4	5	20	0.5	250	

2.4 TERPOLYMER HIGH DIELECTRIC PERMITTIVITY: APPLICATION TO ELECTRIC ENERGY STORAGE

For a non-linear dielectric polymer, the stored and discharged electric energy density should be directly calculated

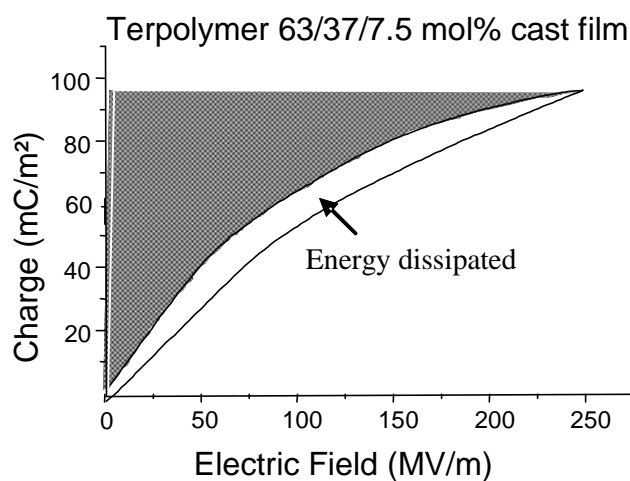


Figure 5. Determination of the discharged (released) energy density (shaded area) and dissipated energy density (open area).

from $U_e = \int E dD$, where D is the surface charge density (electric displacement which is the same as the polarization for the polymers investigated here). Using the polarization hysteresis loop measured under unipolar condition, the stored and discharged energy density can be obtained as schematically shown in Figure 5. This Figure is for the terpolymer measured at 10 Hz and the shaded area is the discharged energy density. The enclosed and unshaded area represents the energy dissipated. The total stored energy density is the summation of the discharged energy density plus the dissipated energy density, from which the efficiency of the dielectric film can be determined.

In the experiment, the applied field E increases from zero to a maximum value (charging the capacitor) and then is reduced to zero (the capacitor discharges). If there is no conduction loss, the charge density at $E=0$ at the end of discharging cycle should be the same as that at the beginning of the charging cycle. Figure 6 presents the charging and discharging curves of the terpolymer 63/37/7.5 mol% measured at 10 Hz under different maximum electric field levels (400 MV/m is the highest field measured). Figures 7 presents the discharged energy density for 63/37/7.5 mol% measured on two samples.

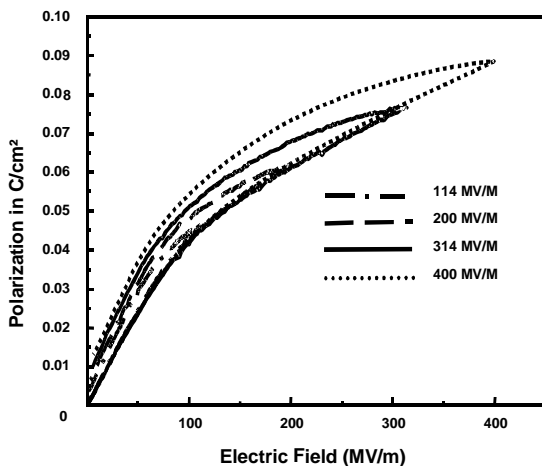


Figure 6. Charging and discharging curves of the terpolymer 63/37/7.5 mol% measured at 10 Hz under different maximum electric field levels.

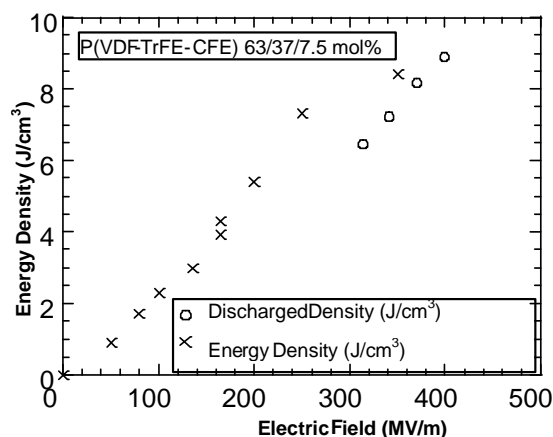


Figure 7. Energy density and discharged energy density for 63/37/7.5 mol% versus maximum electric field levels.

Table 2: Discharge Energy of 63/35/8.5 mol% 63/37/7.5 mol% films

Composition (mol%)	Electric Field (MV/m)	Released Energy (J/cm ³)	Thickness (μm)
65/35/8.5 gold electrode	310	6.03	11
	327	6.43	11
	345	6.81	11
65/35/8.5 Al electrode	310	5.87	11
	327	6.24	11
	345	6.61	11
	360	6.97	11
63/37/7.5 gold electrode	314	6.45	7
	342	7.23	7
	371	8.16	7
	400	8.9	7

Table 2 summarizes data of 63/35/8.5 mol% and 63/37/7.5 mol% films. Part of the data plotted on the Figure 7 is recalled. Especially the values of the energy recovery are given. For the terpolymer film (63/37/7.5 mol%) the electric energy density is equal to 8.9 J/cm³ under 400 MV/m. Figure 8 present the discharged energy density for the terpolymer 68/32/9 mol% which can reach 10 J/cm³ under 350 MV/m.

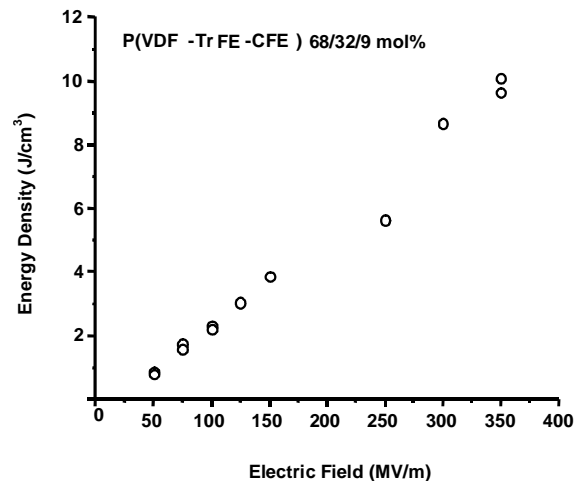


Figure 8. Discharged energy density for 68/32/9 mol% which can reach 10 J/cm³ under 350 MV/M.

As a first step to measure the high voltage high speed discharge characteristics of these terpolymers, a high speed high voltage amplifier circuit was designed and built. Currently, this circuit can handle voltage up to 2.3 kV with a voltage drop to zero to below 0.2 ms. The scheme of the circuit is shown in Figure 9. Using the pulse discharge circuit as shown on the Figure 9, the discharge energy density for the terpolymers was measured into a resistive circuit. The discharge time was 1.25 ms. Electric discharge measurements are summarized in Table 3. These results along with the data in Table 3 indicate that both VDF/TrFE ratio as well as CFE mol% will affect the discharge energy density.

ACKNOWLEDGMENT

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*Present address: Piézotech S.A. 9, rue de Colmar 68220 Héisingue, France.

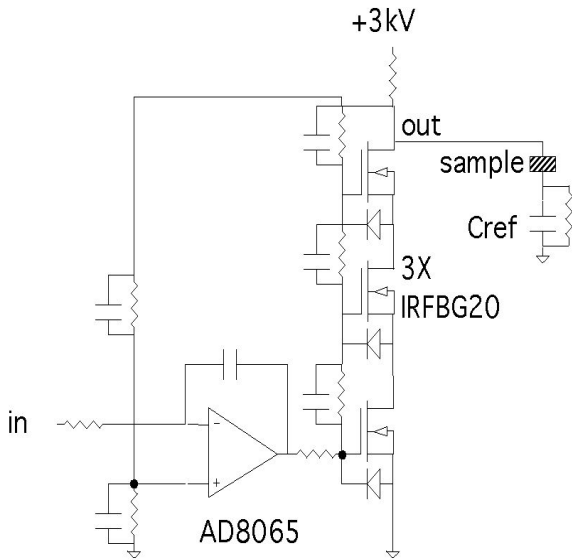


Figure 9. Scheme of the pulse discharge circuit [7].

More characterization over a broad composition range and processing conditions will be needed to establish general guidance on the energy density and efficiency in this class of polymers. It should be pointed out that the data in Table 3 show that at 321 MV/m, the discharged energy density for the terpolymer 63/37/7.5 mol% measured at about 1 ms is 6.64 J/cm³ which is not very much below of that computed from Table 2 and Figure 7.

Table 3: Discharge Energy of ISL-14 (63/37/7.5 mol%) Film

Electric field (MV/m)	Released Energy (J/cm ³)	Falling time (ms)	Film Thickness (μm)
57.1	0.544	1.25	7
116.1	1.646	1.25	7
171.4	2.892	1.25	7
236.6	4.418	1.25	7
283.5	5.515	1.25	7
321.4	6.647	1.25	7

Discharge Energy of ISL-17 (64.3/27.6/8.1 mol%) Film

Electric field (MV/m)	Released Energy (J/cm ³)	Falling time (ms)	Thickness (μm)
50	0.48	1.25	8
100	1.996	1.25	8
150	3.345	1.25	8
200	4.341	1.25	8
225	4.727	1.25	8
250	5.126	1.25	8

CONCLUSION

The class of electroactive polymers P(VDF-TrFE-CFE) offers unique properties in comparison with other polymers. These relaxor-ferroelectric terpolymers P(VDF-TrFE-CFE) are multifunctional i.e. electrostrictive material, dielectric for electric energy storage. High electrostrictive strain leads to large actuation capability. High room temperature dielectric constant (~ 50, to our knowledge, this is the highest among the known polymers), high induced polarization (~ 0.1 C/m²), and high electric breakdown field (>400 MV/m) lead to very high electric energy density for the electric energy storage capacitors.