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Thermal Energy Harvesting Using Fluorinated Terpolymers

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1. Introduction

Energy supply has always been a crucial issue in designing battery-powered wireless sensor networks because the lifetime and utility of the systems are limited by how long the batteries are able to sustain the operation. Therefore, harvesting energy from the environment has been proposed to supplement or completely replace battery supplies to enhance system lifetime and reduce the maintenance cost of replacing batteries periodically. Of the available ambient energy sources, which include, for instance, light energy, mechanical energy, and thermal energy, most innovative solutions deal with energy harvesting from vibration, but very few concern harvesting with temperature variation.

In the last several decades, thermoelectric devices have received significant attention¹. They make use of the Seebeck effect to directly convert a steady-state temperature difference to electricity at the junction of two dissimilar metals or semiconductors. However, the precondition of steady-state heat flow greatly restricts the practical applications. On the contrary, pyroelectric energy conversion directly converting time-dependent temperature variations to electricity could be promising and by applying a proper thermodynamic cycle, a high conversion efficiency would be obtained. Presently, it is found that fluorinated polymers and especially terpolymers have enormous potential for energy harvesting from heat due to its large pyroelectric activity. In 1985, Olsen et al. reported the first pyroelectric conversion cycle for the copolymer P(VDF-TrFE), the output electrical energy density was 30 mJ/cm³, which is 15 times larger than any other polymer previously measured². In 2010, Nguyen et al. developed the pyroelectric energy converter using copolymer 60/40 P(VDF-TrFE) and based on Ericsson cycle³. A maximum energy density of 130 mJ/cm³ was achieved at 0.061 Hz frequency with temperature oscillating between 69.3 and 87.6°C ($\Delta T=18.3^\circ$). In 2011, Navid et al. improved this energy converter by changing the mode of temperature change⁴. They implemented the Ericsson cycle by successively dipping the films in cold and

hot silicone oil baths at 25 and 110°C, and compared three different copolymer samples: commercial purified, and porous films. A maximum energy density of 521 mJ/cm³ and 426 mJ/cm³ per cycle were produced by commercial and purified films, respectively, under applied electric fields ranging between 20 and 50 kV/mm, and a maximum energy density of 188 mJ/cm³ per cycle under electric fields between 20 and 40 kV/mm.

With the development of miniaturization of integration, the aim of energy harvesting is to power smaller and smaller devices, and electrostatic energy conversion is of significant interest and so is suitable for micro-scale electrical power generation. Meninger et al. presented a MEMS (Micro-Electro-Mechanical Systems) vibration to an electricity converter based on electrostatic energy harvesting by a variable capacitor. Mechanical vibrations exert an electrostatic force changing the distance between two electrodes (leading to a variable capacitance)⁵. With an appropriate thermodynamic cycle, Stirling cycle or Ericsson cycle, electrical energy can thus be harvested. In order to avoid the external mechanical force, electrostatic energy harvesting can be performed by nonlinear capacitance variation under temperature variation.

Having taken into account the statement above, a variable capacitance is the critical element for electrostatic energy harvesting. To our best knowledge, the dielectric material can be considered as a capacitor by sandwiched between metallic electrodes, and its dielectric constant is the function of temperature, based on above, we proposed that electrostatic energy harvesting on a relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer, the variable capacitance could be achieved by the dielectric permittivity variation with temperature just below the dipolar transition.

2. Material consideration

2.1. PVDF-based terpolymer

From the basic ferroelectric response consideration, the defect structure modification of the ferroelectric properties can be realized by introducing randomly in the polymer chain a third monomer, which is bulkier than VDF and TrFE monomers. Compared with the high-energy electron irradiation, the terpolymer approach to modify the copolymer from ferroelectric to relaxor is more attractive since it reduces the manufacture cost and significantly simplifies the processing steps. In addition, it greatly reduces the undesirable side effects introduced by the irradiation to the polymers.

Zhang et al. developed a method of converting the polymer to a relaxor ferroelectric by introducing defects into the P(VDF-TrFE) copolymers, i.e., terpolymer containing the chlorofluoroethylene (CFE, -CH₂-CFCl-) or chlorotrifluoroethylene (CTFE) as the termonomer^{6,7}. The introduction of the third monomer into the polymer chain serves to break up the ferroelectric domains into local nano-polar regions surrounded by an amorphous matrix, thereby reducing their size. The resulting nano-polar regions are more mobile and increase the polarization response and overall permittivity. By co-polymerization of CFE or CTFE with the P(VDF-TrFE), the polymer could be converted to a relaxor ferroelectric which

eliminated the polarization hysteresis (dielectric heating) at room temperature associated with the change of polarization⁸. These relaxor-ferroelectric terpolymers P(VDF-TrFE-CFE) and P(VDF-TrFE-CTFE) exhibit a room temperature dielectric constant greater than 50. These values are among the highest ones reported in the literature, and make the terpolymers suitable in our study for energy harvesting by nonlinear capacitance variation.

2.1.1. Terpolymer P(VDF-TrFE-CTFE)

Xu et al. synthesized and evaluated terpolymer P(VDF-TrFE-CTFE) using the bulk polymerization method⁹. As the bulky and less polar monomer CTFE is randomly introduced into P(VDF-TrFE) normal ferroelectric crystals, there are three main features in the dielectric data of the polymer due to the addition of CTFE observed: (1) the original FP transition peak of the copolymer is moved to room temperature; (2) the peak becomes much broader and its position shifts progressively with frequency towards higher temperature; (3) there is no thermal hysteresis in the dielectric data, i.e., the broad dielectric peak stays at the same temperature when measured in the heating and cooling cycles. They also measured the polarization hysteresis loops at room temperature and -40°C⁹. The terpolymer exhibits a slim polarization loop at room temperature, and as the temperature is lowered, the coercive field increases and the polarization at maximum electric field decreases. All these features are remarkably reminiscent of ferroelectric relaxor behaviour. In addition, the polarization reduction when the temperature decreased proved that, at lower temperature range (temperature lower than transition), the dielectric permittivity variation shows overwhelming advantage, while the pyroelectric effect becomes negligible. It gives a strong proof for our study in energy harvesting from capacitance variations by lowering the temperature.

2.1.2. Terpolymer P(VDF-TrFE-CFE)

There were also experimental results on terpolymer P(VDF-TrFE-CFE). Zhang et al. compared the terpolymer P(VDF-TrFE-CFE) with P(VDF-TrFE-CTFE), and concluded that the CFE is more effective on improving their electromechanical response compared with CTFE, shown in the following aspects: (1) In the containing CFE, 4-5 mol% of CFE seems to be adequate to nearly eliminate the polarization hysteresis, while in the terpolymers containing CTFE, nearly 10 mol% is required. (2) P(VDF-TrFE-CFE) 62/38/4 mol% terpolymer exhibits a much higher elastic modulus in comparison with P(VDF-TrFE-CTFE) 65/35/10 mol% terpolymer, resulting in much higher elastic energy density and electromechanical coupling factor in the P(VDF-TrFE-CFE) terpolymer⁶.

Klein et al. revealed that the addition of CFE leads to two types of crystalline regions within the polymer, where a non-polar phase coexists with a polar phase. At high CFE mol% (>8.5 mol%) in the compositions range of VDF/TrFE mole ratio between 64/36 to 75/25, the polar phase region is no longer detectable, indicating a complete conversion to the relaxor ferroelectric phase and the terpolymer exhibits the highest strain level with very little hysteresis. They compared the measured strain as a function of the applied field for two

compositions of 65/35/8.6 mol% and 75/25/5.3 mol%¹⁰. The presence of the polar-phase in the terpolymer of 75/25/5.3 mol% greatly reduces the electrostrictive strain in the polymer. On the other hand, increasing CFE content causes reduction in crystallinity, which will affect the elastic modulus and the induced polarization level of the polymer¹⁰. These competing effects determine the desired terpolymer compositions for given application.

In 2008, Neese et al. studied the other important property on terpolymer P(VDF-TrFE-CFE): electrocaloric effect (ECE)¹¹. Electrocaloric effect corresponds to a reversible change of temperature induced by an electric field under adiabatic conditions. A large ECE requires a large entropy change associated with polarization change, and the dielectric material must be capable of generating large polarization changes. In regard to it, ferroelectric polymers are better than ceramics due to their high dielectric strength. By this way, a large entropy change can be achieved. The relaxor ferroelectric polymers have the potential for processing attractive ECE properties due to their large polarizability, small polarization hysteresis, and dielectric peak near room temperature. Neese et al. concluded that with an electric field of 307 MV/m at 55°C applied on terpolymer P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol%, temperature variation $\Delta T = 12^\circ$ and entropy change $\Delta S = 55 \text{ J/(kgK)}$ were obtained. Especially, the entropy change is about 7 times greater than that in the ferroelectric ceramics¹¹. Their study indicates that the large entropy change can be achieved associated with the electric field-induced dipole ordering – disordering (O-D) processes at temperature near O-D transitions. This transition becomes the critical technique during the process of energy harvesting on terpolymer that we will discuss it in the following part.

In view of the favourable properties above, low ferroelectric hysteresis, the temperature of the dielectric constant peak shifts to room temperature, large polarization variation induced by the O-D transition, high elastic energy density of PVDF-based terpolymer make it attractive for energy harvesting by temperature variation. Moreover, Ren et al.¹² also reported energy harvesting using a ferroelectric polymer, possessing high electromechanical response and elastic energy density, which make it possible to generate high electrical energy density and attractive for the active energy harvesting scheme. This study shows that combining the active energy harvesting scheme and high electromechanical response of the polymer yields a harvested electric energy density of $\sim 40 \text{ mJ/cm}^3$ with a 10% efficiency at very low frequency.

The outstanding properties of electroactive terpolymer, such as high room temperature dielectric constant, high polarization variation induced by temperature, and high electrostriction etc., make it seem to be the promising candidate for active harvesting of energy, no matter from thermal or mechanical energy sources. The investigation of polymers opens up novel possibilities for multi-source energy harvesting technique. In view of thermal energy harvesting, the use of copolymer P(VDF-TrFE) to harvest waste heat by pyroelectricity has been explored both experimentally and theoretically²⁻⁴. In this part, we are interested in energy harvesting from nonlinear capacitance variation by temperature on terpolymer P(VDF-TrFE-CFE)¹³.

3. Energy harvesting by nonlinear capacitance variation for a relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer

3.1. Introduction

In this work, the variable capacitance is realized by the relaxor poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) P(VDF-TrFE-CFE) terpolymer as it exhibits a large nonlinear dielectric constant variation around the dipolar ordering-disordering transition. Benefiting from the application of the Ericsson cycle and the transition at a constant electric field, the harvested energy can be greatly improved. Accordingly, the terpolymer P(VDF-TrFE-CFE) 61.3/29.7/9 mol% is chosen to be the active material of this work.

3.2. Preparation of terpolymer P(VDF-TrFE-CFE)

The terpolymer films were prepared through a solution casting method. The terpolymer P(VDF-TrFE-CFE) 61.3/29.7/9 mol%, supplied by PIEZOTECH, France, was firstly dissolved in N-dimethylformamide by stirring at room temperature for one day. The uniform solution was put in the vacuum for removing the bubbles and then deposited onto a plat of glass by the solution casting method using a doctor blade applicator (Elcometer 3700). Subsequently, the film was placed into the oven at 60°C for one day and was annealed at 85°C for 6 h in a vacuum oven to remove residual solvent. Gold electrodes were sputtered on the two surfaces of the 20- μm films which were stuck to a steel substrate as shown in Fig. 1, for accelerating heat exchange during the temperature variation step of energy harvesting cycle. The results presented below were obtained at least on five samples.

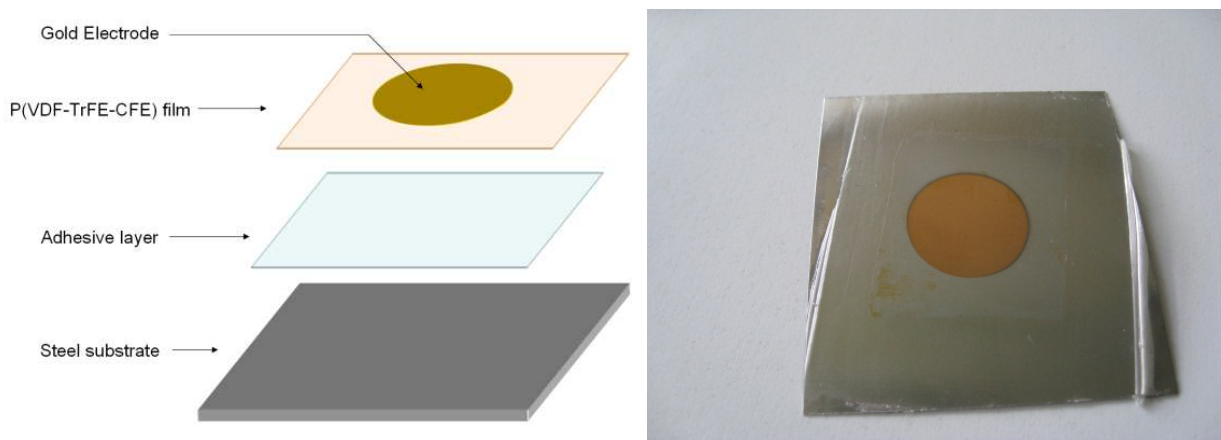


Figure 1. Sample used in this study: P(VDF-TrFE-CFE) terpolymer film stuck to steel substrate.

3.3. Principle of electrostatic energy conversion

Mitcheson et al. has presented generally the electrostatic energy conversion and its two possible conversion cycles: charge constrained and voltage constrained cycles¹⁴. In this part, we focus on the voltage constrained cycle which was used in our work. We put the scheme of cycles below in order to quantitatively discuss the capability of energy harvesting on P(VDF-TrFE-CFE) 61.3/29.7/9 mol% terpolymers.

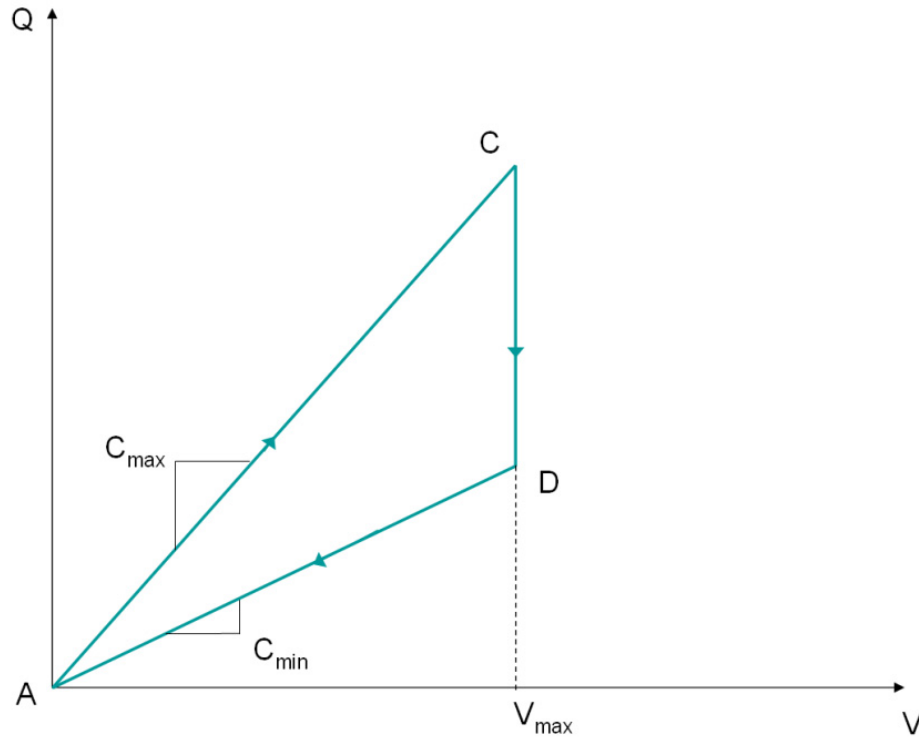


Figure 2. Scheme of electrostatic energy conversion cycles.

In this work, the voltage constrained case was chosen, cycle analogous to the other thermodynamic cycle-Ericsson cycle, which consists of two isothermal and two constant electric field processes¹⁵. The cycle starts when the capacitor is charged up to V_{\max} from reservoir. This is done when the capacitance is at maximum. The injected energy corresponding to the AC segment of the cycle is calculated as

$$W_{\text{inject}} = \frac{1}{2} C_{\max} V_{\max}^2 \quad (1)$$

During this time, the value of capacitor is taken to be constant, and so the segment of A-C is a straight line. This is a valid assumption since the charge-up time to traverse path A-C (and discharge path D-A) is transient, while the segment C-D, which corresponds to the capacitance variation, is relative longer (in our case, the time is equal to that of temperature variation around 20 seconds). It is evident from the Fig. 2. **Error! Reference source not found.** that during this step in the conversion process, the voltage is held constant (hence the name voltage contained conversion.). As the capacitance decreases, path segment C-D is traversed, where the capacitance is at a minimum. In our case, the capacitance is changed by decreasing the temperature of terpolymer, the electrostatic force does work by causing charge to move from the capacitor back into the reservoir. The charge remaining on the plates is then recovered while capacitance of terpolymer reducing to minimum C_{\min} following path D-A, the terpolymer is discharged (D-A). Since the segments C-D and D-A, the energy is harvested from heat to electric power, W_{harvest} , is the area ACD in Fig. 2.

$$W_{\text{harvest}} = -\frac{1}{2}(C_{\text{max}} - C_{\text{min}})V_{\text{max}}^2 \quad (2)$$

This method sets a maximum limit on the conversion process. The major obstacle for this approach is that some method must be employed to hold the voltage across the capacitor of the device during the conversion process, which would require another source of value V_{max} . This is an additional source to that of the conversion charge reservoir, which is of a lower voltage and is also used to power the control electronics.

3.4. Characterization of terpolymer P(VDF-TrFE-CFE)

As mentioned earlier, the discovery of high electromechanical performance in P(VDF-TrFE-CFE) based terpolymer opens a new avenue for developing high performance electroactive polymers. Also, by introducing the termonomer, for example CFE, to form P(VDF-TrFE) based terpolymer, the normal ferroelectric P(VDF-TrFE) could be converted into a ferroelectric relaxor with high room-temperature dielectric constant peak and a very slightly polarization hysteresis. In a consequence, the terpolymer P(VDF-TrFE-CFE) 61.3/29.7/9 mol% was processed, and the characterization would be investigated in detail in this part.

3.4.1. Dielectric and ferroelectric characterization

The weak field dielectric properties were measured as a function of temperature by an impedance/GAIN-phase Analyzer (HP4194A). The terpolymer films (20 μm -thickness) stuck onto the steel substrate was put into a controlled temperature chamber and connected with an impedance/GAIN-phase Analyzer. Fig. 3 shows the temperature- and frequency-dependent dielectric constant and loss tangent of terpolymer. As expected, due to the introduction of defect structure, the sharp dielectric constant peak in copolymer turns into a broad peak in terpolymer, and the O-D transition peak is moved to around room temperature. Especially, the broad dielectric peak position of dielectric constant shifts slightly with the frequency towards higher temperature⁶, such a behaviour is a typical feature to all the known relaxor ferroelectric materials.

As seen in Fig. 3, it indicates that the dielectric constant shows a maximum at nearly room temperature, and decreases more rapidly at the lower temperature range than that at the higher temperature range, the large dielectric constant variation can result in the large electrical displacement variation. On the other hand, Xu et al. have confirmed that the pyroelectric effect could be ignored at this temperature range⁹. Consequently, the high nonlinearity of dielectric permittivity (capacitance) together with the negligible pyroelectric effect could be an important favourable factor for harvesting energy in our study.

In order to investigate the temperature effect of basic ferroelectric characterization on terpolymer, we measured the ferroelectric hysteresis loops at different temperature as shown in Fig. 4. D-E loops were carried out every 5°C between 20°C and -20°C in descending order, and the unipolar sine electric field was applied with the average slope of $dE/dT=40000 \text{ kV mm}^{-1}\text{s}^{-1}$ which is the same slope with the bipolar cycle at 100 Hz. This frequency was chosen due to its lower hysteresis loss than other frequency.

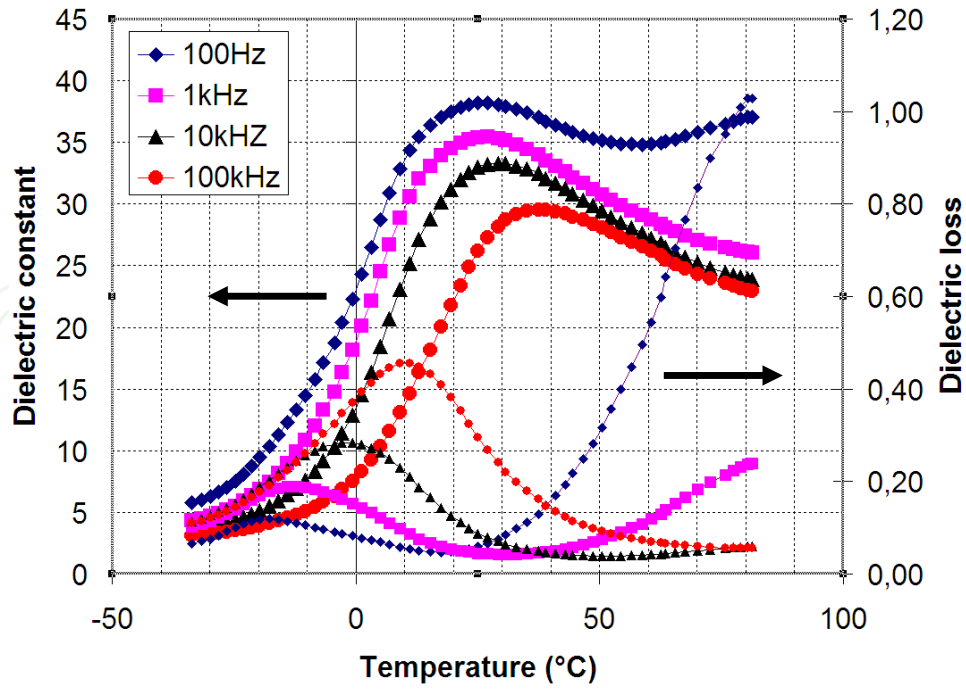


Figure 3. Temperature dependence of weak field dielectric properties of terpolymer P(VDF-TrFE-CFE) measured at different frequencies.

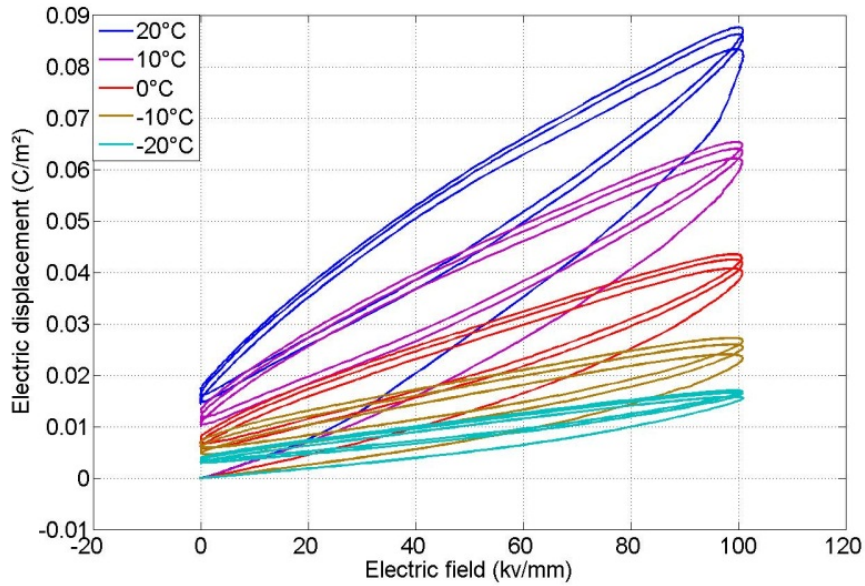


Figure 4. Unipolar D-E loops at different temperature under 100 kV mm^{-1} .

Fig. 4 presents that the electric displacement displays an obvious reduction with the decrease of temperature under the maximum electric field 100 kV mm^{-1} , it is consistent with reduction of the dielectric constant in Fig. 3. As we know, there exists two kinds of polarization mechanism in the relaxor ferroelectrics: thermally activated flips of the nanopolar regions at high temperature and the breathing of frozen nanopolar regions at lower temperature¹⁶. In the relaxor ferroelectric terpolymers, since the temperature lowered

from high temperature to the temperature of the dielectric constant peak, the population of the nanopolar regions increases. The polarization response under high electric field is mainly obtained from the relaxation polarization which is associated with the thermally activated flips of the nanopolar regions. Around the temperature of the dielectric constant maximum, the polarization behavior reaches the maximum due to the largest quantity of the thermally active nanopolar regions. Further lowering the temperature, partial nanopolar regions become frozen, polarization behaviour is mainly determined by the breathing of the frozen nanopolar regions. The large electric displacement variation is achieved due to the nanopolar regions transition from thermally activated flip behaviour to breathing behaviour. Take the two extreme cases for instance in our measurement, at 20°C, the thermally activated flips of the nanopolar regions are predominant, so the large polarization response could be observed, as shown in Fig. 3, the electric displacement comes up to 0.086 C/m². Lowering the temperature down to -20°C, the breathing of frozen nanopolar regions is predominant, although still the same electric field, the electric displacement is just 0.017 C/m². The variation of electric displacement is satisfactory for harvesting energy.

3.5. Electrostatic energy harvesting by nonlinear capacitance variation for a relaxor ferroelectric P(VDF-TrFE-CFE)

Based on the characterization mentioned above, we indicate that, as relaxor ferroelectric terpolymer P(VDF-TrFE-CFE) 61.3/29.7/9 mol% is a promising candidate for electrostatic energy harvesting on Ericsson cycle by nonlinear capacitance variation, due to the high non-linear property of the dielectric constant in the vicinity of the polarization mechanism transformation.

3.5.1. Experiment setup

A waveform generator (Agilent 33220A), a high voltage amplifier (TREK Model 10/10B) and a current preamplifier (STANDFORD Model 570) were used to determine the dielectric constant under a DC electric field and to carry out the Ericsson cycle. An elaborate sample holder with closed protecting-cell is used to fix the sample, protect the polymer during the temperature change and applying the external electric field.

3.5.2. Theoretical model

An Ericsson cycle can be used for harvesting energy^{3,15,17}. It consists of two isothermal processes (charge at θ_1 and discharge at θ_2) and a process for cooling the sample from θ_1 to θ_2 under a constant electric field. Assuming that there is a linear relationship between the electric field and the dielectric displacement:

$$D = \varepsilon_{33}(\theta)E \quad (3)$$

Where $\varepsilon_{33}(\theta)$ and θ , denote respectively the permittivity and temperature. The injected energy during the charging process (applied electric field from 0 to E_1) is given by

$$W_{\text{inject}} = \int_0^{E_1} E dD \quad (1)$$

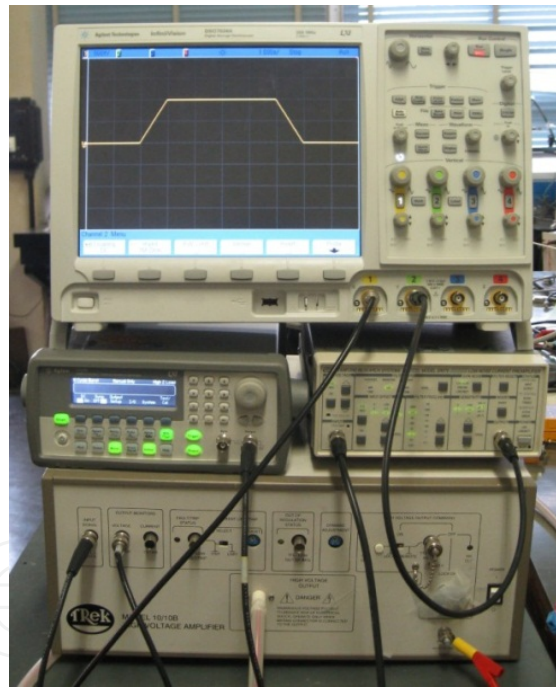
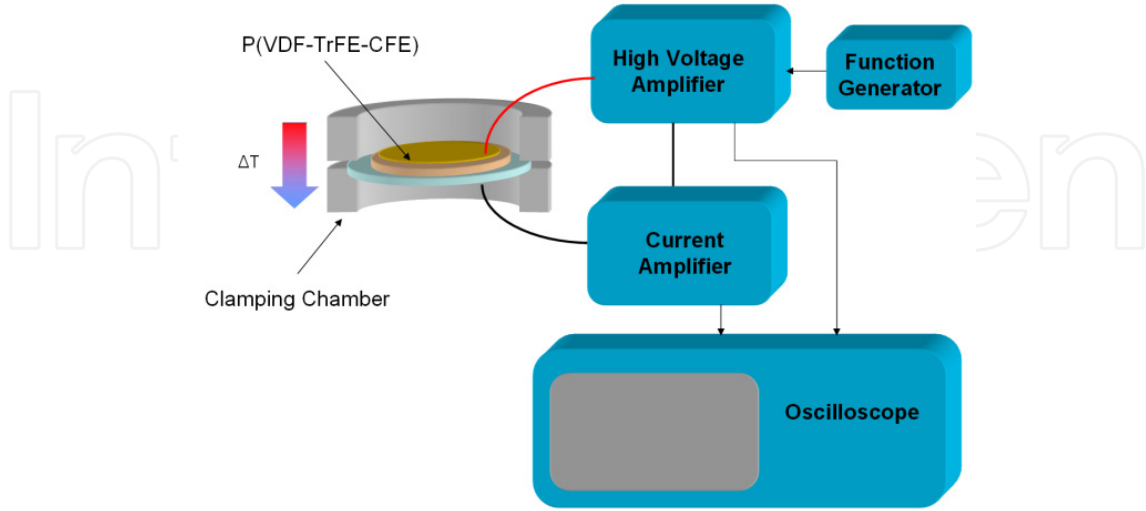


Figure 5. A schematic (upper) and a picture (lower) of the experimental setup for measuring the energy harvesting system in the terpolymers.

After the discharging process, the electric displacement returns to zero. Here, the other constant electric field process of the Ericsson cycle no longer exists since there is no remnant polarization for relaxor ferroelectrics. The whole cycle is described in a clockwise path leading to harvested energy which is equal to the area of the cycle:

$$W_{\text{harvest}} = \oint E dD \quad (5)$$

When changing the electric field and the temperature of a relaxor material, electrocaloric¹⁸ (change in temperature induced by the application of an electric field) and pyroelectric (change in electric polarization induced by a temperature variation) effects¹⁹ inevitably occur, but, in the present study, both were negligible. The electrocaloric effect was too small to change the temperature of the terpolymer in a significant manner (maximum 1K for the electric field applied in this study)¹¹. Similarly, the pyroelectric effect, during cooling from 25°C to 0°C, was too low to lead to a significant increase of the electric displacement as described in the work performed by Xu et al.⁹ where the electric displacement was remarkably decreased for a relaxor terpolymer when going from room temperature to a lower temperature.

Assuming that, theoretically, the permittivity is constant during the charging and discharging processes, the injected and harvested energy can be expressed as follows:

$$W_{\text{inject}} = \frac{1}{2} \epsilon_1 E_1^2 \quad (6)$$

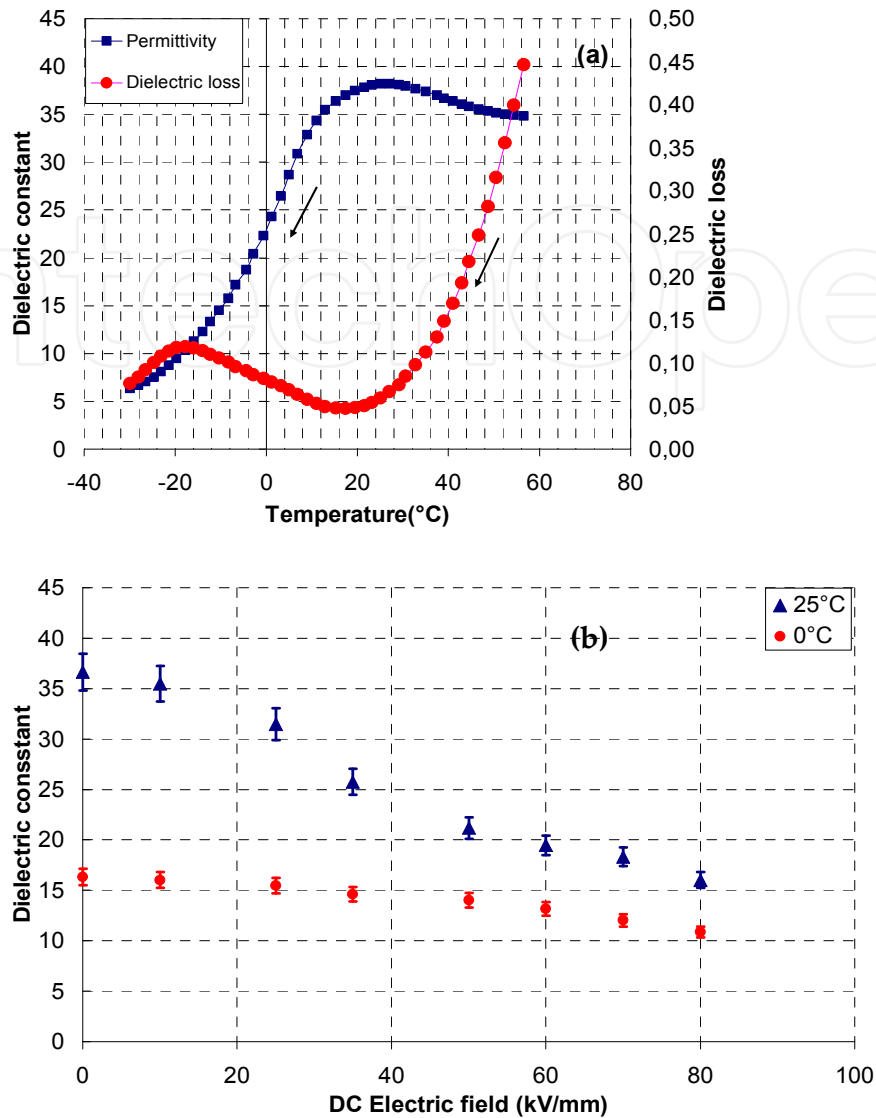
$$W_{\text{harvest}} = -\frac{1}{2} (\epsilon_1 - \epsilon_2) E_1^2 \quad (7)$$

where ϵ_1 and ϵ_2 are the permittivity during the charging and discharging processes, respectively.

3.5.3. Results and discussion

The theoretical analysis indicates that the harvested energy mainly depends on the capacitance variation, which in turn depends on the temperature. Fig. 6(a) shows the weak field dielectric properties (measured at 100 Hz) as a function of temperature, which has been verified on five samples. The permittivity demonstrated a maximum at the transition temperature (25°C), and then decreased rapidly in the lower temperature range. Benefiting from this transition, a large capacitance variation was obtained. According to these results, the temperatures of 25°C and 0°C were chosen as the charging and discharging temperatures, respectively, for the Ericsson cycle. The time for charging and discharging the sample corresponds to a frequency of 100 Hz in order to compare simulation and experiment without frequency effect.

The terpolymer was under a DC electric field during the temperature change in the Ericsson cycle. Lu et al. showed that the permittivity of PVDF-based polymers (poly vinylidene-fluoride) exhibits a tunability under a DC electric field²⁰. This tunability is a function of temperature, especially in the vicinity of the dielectric peak where the polymer has the largest tunability. Therefore, the dielectric constant (relative permittivity) was measured under different DC electric fields (E_{DC}) with a small AC field (E_{AC}) at 100 Hz and at 25°C and 0°C, as shown in Fig. 6(b). The experimental uncertainties correspond to a 95% confidence interval. Two main points are emphasized: (1) it existed a tunability of the permittivity under a DC electric field (the tunability was larger at 25°C than at 0°C) and (2) this tunability presented a non linear behavior with temperature.



(a) dielectric constant (black squares) and dielectric loss (red circles) as a function of temperature under a weak field, (b) dielectric constant under a DC electric field at 25°C (blue triangles) and 0°C (red circles).

Figure 6. Dielectric property on P(VDF-TrFE-CFE) 61.3/29.7/9 mol%.

As the DC electric field increased from zero to 80 kV/mm, the capacitance variation between 25°C and 0°C decreased significantly (the dielectric constant variation was 21 at $E_{DC}=0$, and 5 at $E_{DC}=80$ kV/mm, corresponding to a reduction by 75%). In physical terms, this can be understood as there existing no macroscopic domain for relaxor ferroelectrics and the polarization mainly depending on the thermally activated flips of the nanopolar regions²¹. An external electric field cannot produce a large domain reorientation, just an alignment of nanopolar regions along the field. At the dielectric peak temperature of 25°C, the quantity of the thermally active nanopolar regions was at a maximum. Nevertheless, at the lower temperature, i.e., 0°C, a majority of the nanopolar regions became frozen¹⁶; the dielectric behavior thus mainly received contributions from the shape change of the frozen polar regions due to the external DC electric field. Consequently, the tunability was larger at 25°C.

The Ericsson cycle was simulated from the measurements of permittivity presented in Fig. 6 and by using Eq. (7). Fig. 7 shows the harvested energy versus the DC electric field considering or not the tunability of the dielectric constant with the electric field. Measurements were undertaken on five samples and the discrepancy is around 10%. The two simulation results almost coincided in the lower electric field range, i.e., at 10 and 25 kV/mm, but at higher electric field, the difference became increasingly pronounced, reaching 46% at 80 kV/mm. These simulations underlined that the tunability needed to be taken into account in order to avoid an overestimation of the harvested energy, especially for high DC electric fields. The harvested energy increased with the maximum DC electric field, and from simulation, a maximum energy of 240 mJ/cm³ could be harvested at 80 kV/mm. However, electrical conduction and the electric field breakdown (lower with electrical conduction) are two inevitable factors, which restricted the experimental harvested energy, need to be resolved.

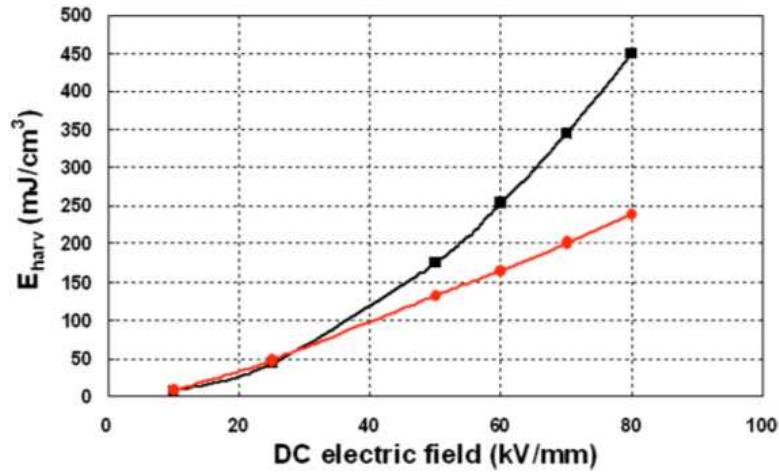


Figure 7. Harvested energy as a function of the DC electric field by a simulated Ericsson cycle for the terpolymer P(VDF-TrFE-CFE) 61.3/29.7/9. Harvested energy simulated by permittivity under a DC field (red circles) and permittivity without a DC field (black squares).

In order to confirm the simulation experimentally, an experimental Ericsson cycle was also undertaken. The energy in each segment could be obtained by the electric field integral with respect to current. Fig. 8 presents the simulated and experimental Ericsson cycles at 25 kV/mm. The direct measurement of the Ericsson cycle was carried out with a slope of $dE/dt=25\text{ kV/mm.s}$ for the charging and discharging processes. The experimental measurement showed the same type of closed Ericsson cycle as the simulation considering the tunability of the dielectric constant. For the experimental cycle, the conduction of the terpolymer is observed while the DC electric field was applied during the temperature change. An Arrhenius law was used to remove the conduction from the experimental data. Fig. 8 presents the experimental Ericsson cycle after eliminating the conduction. The harvested energy was computed by Eq. (12), and was found to be 50 mJ/cm³, which was consistent with the simulation (48 mJ/cm³). The experimental Ericsson cycle was performed over several cycles on five samples and gave nearly the same harvested energy with a deviation of 10%, as well as simulation, it is the same deviation for harvested energy due to that on dielectric constant, the most representative cycle was chosen corresponding to the average of measured cycles.

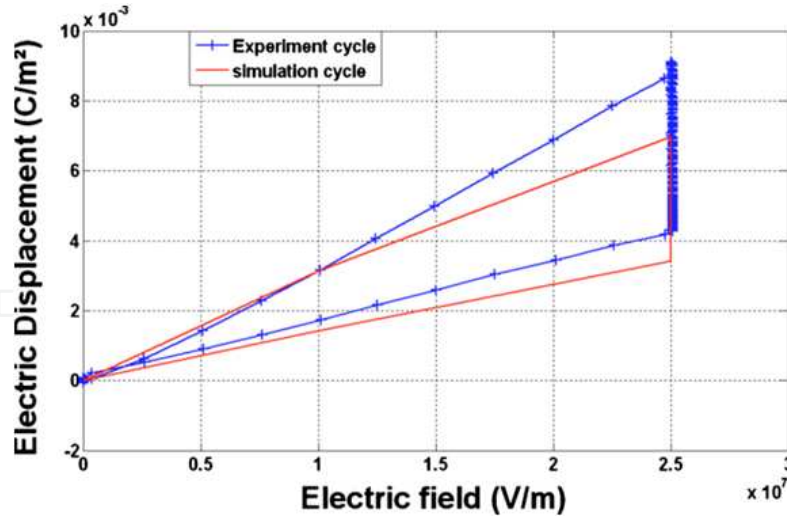


Figure 8. Simulated Ericsson cycle using a dielectric constant (red circles) and its experimental counterpart (blue crosses) for P(VDF-TrFE-CFE) 61.3/29.7/9 mol%.

4. Conclusion

PVDF-based polymer was introduced in detail in this chapter, especially for terpolymer P(VDF-TrFE-CFE). By copolymerizing the P(VDF-TrFE) with a third monomer to form a terpolymer, the defects introduce inhomogeneity in the ferroelectric phase which broadens the transition region and reduce or eliminate the hysteresis. As a result, the normal ferroelectric is transformed into a relaxor ferroelectric polymer. Due to the high room-temperature dielectric peak and slightly polarization hysteresis, terpolymer P(VDF-TrFE-CFE) 61.3/29.7/9 mol% was chosen as the active material for electrostatic energy harvesting. In addition, the basic electrostatic energy harvesting cycles -- voltage constrained cycle, was studied. The main work concentrated on Ericsson Energy Harvesting by Nonlinear Capacitance Variation between 25°C and 0°C.

In this part, we presented our work on thermal energy harvesting by electrostatic technique. It was realized by utilizing the nonlinear capacitance variation of relaxor terpolymer P(VDF-TrFE-CFE). We prepared the terpolymer through the solution casting method, and then, we investigated their characterization in detail, including dielectric properties and the temperature effect of basic ferroelectric properties. In order to simulate the harvested energy accurately, we also studied the tunability of the dielectric constant of the terpolymer.

The weak field dielectric properties were measured in order to determine the working temperature during Ericsson cycle. The largest variations in capacitance were obtained between 25°C and 0°C due to a dipolar ordering-disordering transition. In order to evaluate the harvested energy by simulation, the dielectric permittivity under DC electric field was also measured and exhibited tunability of dielectric constant as a function of temperature. Especially in the vicinity of the dielectric peak, the tunability expressed more obviously. This phenomenon was analyzed and explained perfectly from the viewpoint of nanopolar regions.

By characterizing the tunability of the dielectric constant under DC electric field, the simulated harvested energy, between 25°C and 0°C under 80 kV/mm, was equal to 240

mJ/cm³. The direct measurement of Ericsson cycle was also carried out with a maximum electric field of 25 kV/mm. When subtracting the conduction, the harvested energy was equal to 50 mJ/cm³ which was consistent with the simulation (48 mJ/cm³). It proved the reliability of our theoretical evaluation and experimental feasibility in practice.

Electric conduction and the electric field breakdown are two inevitable negative factors, which restricted the experimental harvested energy, need to be resolved. The next work aims to improve the quality of polymer so as to overcome these restrictions of the experiment. Previous work dealt with the purification of a P(VDF-TrFE) copolymer and the effect of the porosity of the film. It appears that the presence of residual solvent or pores inside the film reduces its resistivity by one order of magnitude²². Fujisaki et al. stated that the conduction emerging at a 'defect' part (TrFE and CFE) was much smaller in amorphous regions as compared to in crystal grains²³. Therefore, it can be reduced by optimizing the proportion of the crystal grains and amorphous regions in the mixture and their respective distribution in the film. In addition, the interface between the film and the electrode also plays an important role for the film's conduction. The improvement of the process of the film is in progress.

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