APPROACHES TO ACHIEVE SMARTER ELECTROACTIVE MATERIALS
AND DEVICES

A Thesis in

Electrical Engineering

by

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ABSTRACT

In the last several decades, considerable research efforts have been devoted to the smart materials, including piezoelectric and electrostrictive ceramics, electroactive polymers (EAP), magnetostrictive materials, shape-memory materials, and magnetorheologic fluids. This has led to the development of several novel materials with high performance. It is the objective of this thesis to explore and expand these new opportunities. Especially, we will investigate and develop innovative approaches to address three applications:

In chapter 2 and chapter 3, the energy harvesting using both the electrostrictive PVDF based polymers and 1-3 single crystal PMN-33PT/Epoxy composite are investigated. In addition to the high elastic energy density and high electromechanical conversion efficiency of these active materials, this study also explores the approaches of using smart electronics to significantly enhance the efficiency of the energy harvesting process. As an example, we demonstrate that when a properly phased and externally applied electric AC field is superimposed on the mechanical cycle, an output electrical energy density of 39mJ/cm³ and mechanical-to-electrical conversion efficiency of about 10% can be obtained from the P (VDF-TrFE) based electrostrictive polymers. For 1-3 single crystal PMN-33PT/Epoxy composite, under a mechanical stress of 88.9 MPa at 4 Hz, a harvested energy density of near 0.1 W/cc can be achieved.

In chapter 4, the Braille actuators suitable for refreshable full page display and graphic display using the electrostrictive PVDF-based polymers are investigated. The current refreshable Braille display utilizes the piezoceramic actuator and the small strain
level requires that the actuator is operated in the bimorph mode, resulting in a bulky device, low reliability, and not suitable for full page refreshable Braille display. An EAP compact Braille actuator was designed and fabricated with PVDF-TrFE-CFE terpolymer films wound on a spring core. The test results demonstrate that the EAP Braille actuator meets all the functional requirements of actuators for refreshable full Braille display, which offers compact size, reduced cost and weight.

In chapter 5, we investigate the hybrid SMP/EAP actuator to create a new class of actuator which can maintain the high strain without electrical signal stimulus and can be reconfigured to different strain and shape. Since the strain generation and elastic modulus of two independent processes, this new actuator has the potential to reach much higher elastic energy density than any of the current solid state actuator materials.

In the following, we will briefly introduce the smart materials to be investigated in my thesis.
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CHAPTER 1
INTRODUCTION

Smart materials are a class of materials that can significantly change their mechanical (such as shape, stiffness, and viscosity), electric, thermal, optical, magnetic, electromechanical or electromagnetic properties in a predictable or controllable manner in response to their environment. These materials include piezoelectric and electrostrictive ceramics, electroactive polymers (EAP), magnetostrictive materials, shape-memory materials, and magneto-rheologic fluids. Sensors and actuators are the devices fabricated by smart materials to make the system “smart”. Sensors are the devices which can detect the environmental stimuli, and sensitivity is the main issue to be considered. Conversely, actuators are designed to respond to environmental stimuli and perform with mechanical responses such as shape change, mechanical motion, force and displacement.

Actuators can be classified into two types: conventional actuators and solid state actuators. Table 1-1 provides a detailed classification of the actuators. The conventional actuators can be divided into three groups: 1) hydraulic pressure type, 2) electromagnetic motor type, 3) electromagnetic coil type. As compared with the solid state actuator, these actuators have the advantage of good controllability and large generated force. However, they are difficult to miniaturize and require high input electrical energy.
Table 1-1: The classification of Actuators

**ACTUATORS**

(1) Conventional Actuator
   a) Hydraulic/Pneumatic Actuator
   b) Electromagnetic Motor
   c) Magnetic Coil (Speaker) (Magnetostrictive)

(2) Solid State Actuator
   a) Thermal Drive (Ferroelastic)
      (Shape Memory)
   b) Magnetic Drive
   c) Electrical Drive
   d) Light Drive (Ferroelectric)
      (Piezo/Electrostrictive)
      (Electrostatic Devices)

**Solid State Actuator Designs**

(a) Longitudinal Strain Actuator
   o Single Layer
   o Multilayer
   o Multilayer-Multistacked

(b) Flextensional Actuator
    Moonie & Cymbals
    o Single layer
    o Multilayer
    o Multilayer-Multistacked

d) Piezomotors

e) Inchworms

f) Torsional Motions

g) Transverse Strain Actuator

(c) Bending Strain Actuator
   o Monomorph
   o Unimorph
   o Bimorph
   o RAINBOW
   o Multilayer
Depending on the driving mechanism, solid state actuators can be classified into three divisions, specifically magnetic actuators (ferromagnetic effect), thermal drive actuators and electrical drive actuators. The most frequently used actuators are electrically driven actuators, which include piezoelectric, electrostrictive and electrostatic actuators.

In the last several decades, considerable research efforts have been devoted to smart materials. These efforts have led to the development of several novel materials with high performance. It is the objective of this thesis to explore these materials and expand on these new opportunities. Specifically, we will investigate and develop innovative approaches to address three applications:

- Energy harvesting using both the electrostrictive poly(vinylidene fluoride) (PVDF) based polymers and 1-3 single crystal PMN-33PT/Epoxy composite (PMN= Pb(Mg\(_{1/3}Nb_{2/3}\))O\(_3\); PT=PbTiO\(_3\)). In addition to the high elastic energy density and high electromechanical conversion efficiency of these active materials, this study also explores the approaches of using smart electronics to significantly enhance the efficiency of the energy harvesting process (active energy harvesting).

- Braille actuators suitable for refreshable full page display and graphic display using the electrostrictive PVDF-based polymers. The current refreshable Braille display utilizes piezoceramic actuators and the small strain level requires that actuators are operated in the bimorph mode, resulting in a bulky device, low reliability, and poor suitability for full page refreshable Braille displays. In this study, various issues related to the electrostrictive PVDF based polymer, such as conducting polymer electrode development, self-healing in electrical breakdown, are investigated.
Hybrid SMP/EAP actuators to create a new class of actuators which can maintain the high strain without external stimulus and can be reconfigured to different strain and shape. Since the strain generation and elastic modulus are two independent processes, this new actuator has the potential to reach much higher elastic energy density than any of the current solid state actuator materials.

In the following section, I will briefly introduce the smart materials to be investigated in my thesis.

1.1 The PVDF based Ferroelectric and Electrostrictive Polymers

1.1.1 The ferroelectric polymer PVDF and copolymer PVDF-TrFE

PVDF based ferroelectric and electrostrictive polymers are semicrystalline polymers in which the crystal phase is imbedded in the amorphous matrix. The semicrystalline morphology of this class of polymers is illustrated in Figure 1-1. The most widely used PVDF based polymers include polyvinylidene fluoride (PVDF), copolymers of PVDF with trifluoroethylene (TrFE) and chlorotrifluoroethylene (CTFE), and terpolymers of P(VDF-TrFE) with a third bulky monomer such as chlorofluoroethylene (CFE) and CTFE and hexafluoropropylene (HFP).
There are at least four different crystal structures possible for PVDF and its copolymers, including the α phase, β phase, γ phase, and δ phase. Among them, the α phase and the β phase are the most common phases for PVDF.9

In typically prepared PVDF homopolymers, the crystalline phase consists of a sequence of alternating Trans and Gauche bond orientations, or TGTG conformation, which is called the α phase. A diagram of the α phase is shown Figure 1-2. By uniaxial stretching, the α phase of PVDF is converted to the β phase, where two chains in an all-trans planar zigzag conformation and the dipole moment of each fluorine-carbon bond are in the same direction, as shown in Figure 1-3.8 Thus, the β phase is a polar phase and the polymer can be poled under high electric field to a piezoelectric state where all crystal domains align.

Figure 1-1: The semi-crystalline structure of piezoelectric polymer PVDF 4
Figure 1-2: A schematic view of α-phase of PVDF having lattice dimensions of $a = 4.98 \text{ Å}$, $b = 9.84 \text{ Å}$, and the chain direction or fiber axis $c = 4.62 \text{ Å}$. 

Figure 1-3: A view of form I, i.e., β phase (trans), having lattice dimensions of $a = 8.58 \text{ Å}$, $b = 4.91 \text{ Å}$, and the chain direction or fiber axis $c = 2.56 \text{ Å}$.
An important phenomenon of PVDF-TrFE is that when the concentration of PVDF is between 50 % and 82 %, there is a distinct ferroelectric-paraelectric (F-P) phase transition below the melting temperature ($T_m$), which can be observed by DSC. When the concentration of the PVDF is larger than 82 %, PVDF-TrFE shows the ferroelectric phase until melting. The phase diagram of the PVDF-TrFE copolymer is shown in Figure 1-4. In the PVDF film, the F-P transition means that polymer structure is changed from $\beta$ phase (all $Trans$) to $\alpha$ phase ($Trans$-$Gauche$). During the F-P phase transition a very large dimension change also occurs.

Moving from Figure 1-2 and Figure 1-3, as compared with the $\alpha$ phase, in the $\beta$ phase there is a larger lattice constant along the chain direction (c direction) and a smaller lattice constant in both a and b direction. Tashiro et al. measured a large lattice strain from the low-temperature (LT) ferroelectric phase to high-temperature (HT) paraelectric phase. Figure 1-5 shows the lattice strain of PVDF-TrFE 65/35 along the polymer chain direction ((001) reflection) and perpendicular to the chain ((200,110)). From the data, the lattice strain along the chain direction ((001) reflection) has -10% strain and perpendicular to the chain direction ((200,110)) has a 7% strain, which is much larger than the strain of PVDF in the electric field.
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From Figure 1-5, PVDF-TrFE shows a large strain associated with the phase transition from the ferroelectric phase to the paraelectric phase (F-P) as the temperature change. Relative to the strain under electrical field, this strain associated with the temperature change is much larger. Previous researchers have explored this area in depth.

In 1988, Tashiro et al. measured the macroscopic strain of PVDF-TrFE 65/35 copolymer. The macroscopic dimension change $\Delta L$ can be expressed as:

$$\Delta L = \Delta L_c + \Delta L_a$$  \hspace{1cm} \text{Eq. 1.1}

where $L_c$ and $L_a$ are the length of crystalline and amorphous phase along the stretching direction, respectively. Thus, the total strain is expressed as:

$$\frac{\Delta L}{L} = \frac{\Delta L_c}{L_c} \frac{L_c}{L} + \frac{\Delta L_a}{L_a} \frac{L_a}{L}$$  \hspace{1cm} \text{Eq. 1.2}

Eq. 1.2 can also be written as:

$$S = S_c x + S_a (1-x)$$  \hspace{1cm} \text{Eq. 1.3}

where $S$, $S_c$ and $S_a$ is the total strain, the crystalline phase strain and amorphous phase strain, respectively. $x$ is the degree of the crystallinity.

The total macroscopic strain of the stretched PVDF-TrFE 65/35 is shown in Figure 1-6.
From Figure 1-6, the total strain of PVDF-TrFE from the F-P transition is about 3.3 %, which is much smaller than the lattice constant change (10 %) found in Figure 1-5. The reason for this is that amorphous phase expands during the heating process, which will partially cancel the strain of crystal phase during the phase transition. We suppose a crystallinity of 50 %. From Eq. 1.3, the amorphous change is about -3.2 %, which is consistent when compared to the general polymer.  

Figure 1-6: Stress dependence of thermal contraction curve of the VDF 65% copolymer.
Table 1-2 summarizes the typical piezoelectric, dielectric, and elastic properties of PVDF and P(VDF-TrFE) 75/25.\textsuperscript{10,14} From this table, it is evident that PVDF and its copolymer show lower piezoelectric coefficient and electromechanical coupling factor (electromechanical properties) as compared with piezoceramics. Furthermore, for many electromechanical applications, an electroactive material with much higher strain level and elastic energy density than the piezoceramic and piezoelectric polymers is required.

Table 1-2: Piezoelectric, dielectric, and elastic properties of PVDF and P(VDF-TrFE) 75/25.\textsuperscript{15}

<table>
<thead>
<tr>
<th>Material parameter</th>
<th>PVDF</th>
<th>P(VDF-TrFE) 75/25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{31}$ (pC/N)</td>
<td>28</td>
<td>10.7 0.18</td>
</tr>
<tr>
<td>$d_{32}$ (pC/N)</td>
<td>4</td>
<td>10.1 0.19</td>
</tr>
<tr>
<td>$d_{33}$ (pC/N)</td>
<td>-35</td>
<td>-33.5 -0.65</td>
</tr>
<tr>
<td>$d_{15}$ (pC/N)</td>
<td></td>
<td>-36.3 -0.32</td>
</tr>
<tr>
<td>$s_{11}$ (10\textsuperscript{10} Pa\textsuperscript{-1})</td>
<td>3.65</td>
<td>3.32 0.1</td>
</tr>
<tr>
<td>$s_{22}$ (10\textsuperscript{10} Pa\textsuperscript{-1})</td>
<td>4.24</td>
<td>3.24 0.07</td>
</tr>
<tr>
<td>$s_{33}$ (10\textsuperscript{10} Pa\textsuperscript{-1})</td>
<td>4.72</td>
<td>3.00 0.07</td>
</tr>
<tr>
<td>$s_{12}$ (10\textsuperscript{10} Pa\textsuperscript{-1})</td>
<td>-1.10</td>
<td>-1.44 -0.036</td>
</tr>
<tr>
<td>$s_{13}$ (10\textsuperscript{10} Pa\textsuperscript{-1})</td>
<td>-2.09</td>
<td>-0.89 -0.022</td>
</tr>
<tr>
<td>$s_{23}$ (10\textsuperscript{10} Pa\textsuperscript{-1})</td>
<td>-1.92</td>
<td>-0.86 -0.022</td>
</tr>
<tr>
<td>$\varepsilon_{33}/\varepsilon_0$</td>
<td>15</td>
<td>7.9 0.09</td>
</tr>
<tr>
<td>$k_{33}$</td>
<td></td>
<td>0.23</td>
</tr>
<tr>
<td>$k_{13}$</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>$k_t$</td>
<td>0.144</td>
<td>0.196</td>
</tr>
</tbody>
</table>
PVDF-TrFE copolymers have been modified through two ways. One is high energy irradiation and the other is synthesizing the copolymer with a third monomer to become terpolymer. We will introduce these two methods step by step.

1.1.2 Irradiated PVDF-TrFE copolymer

One method of improving the electromechanical property is to add a defect into the structure of the PVDF-TrFE to reduce the energy barrier from the one polarization direction to another or when transforming from one phase to another and thereby improve the electromechanical response. In this way, one can convert the PVDF based copolymer from a normal ferroelectric polymer to a relaxor ferroelectric polymer and dramatically improve the electric field induced strain as well as lower the Curie transition temperature and thereby enhance electromechanical conversion efficiency. The material would become a high strain and high elastic energy density material, which is the highly desirable for the electromechanical applications.

In 1998, it was discovered that high energy electron irradiation on P(VDF-TrFE) copolymer can induce the change in ferroelectric properties and result in a giant electrostriction. The dielectric properties of the irradiated PVDF-TrFE are shown in Figure 1-7. From the data, the temperature of the maximum dielectric constant (T_m) shifts progressively towards higher temperature with frequency, which is a special characteristic of relaxor ferroelectric materials. The hysteresis loop was also measured with temperature. The comparison of PVDF-TrFE with irradiated PVDF-TrFE copolymer is shown in Figure 1-8. For the irradiated copolymer PVDF-TrFE, the hysteresis loop is
much slimmer relative to the PVDF-TrFE copolymer. This is another piece of evidence that the irradiated copolymer PVDF-TrFE is a relaxor ferroelectric polymer.

The irradiated copolymer exhibits very large electrostriction and the longitudinal and transverse strain of the irradiated stretched copolymer is shown in Figure 1-9 and Figure 1-10, respectively. Relative to ferroelectric PVDF, the strain is also much larger. The electrostrictive coefficient $M$, defined as $S=ME^2$, can be $3 \times 10^{-18}$ m/V under a field of 100 MV/m. From the expression relating polarization to E-field, the strain is proportional to the square of the dielectric constant ($S \propto K^2$). Meanwhile, for the irradiated PVDF-TrFE, the dielectric constant is greatly enhanced. This may indicate the origin of the high electrostrictive strain of the relaxor ferroelectric polymer.

The electrostrictive polymer can be treated as a piezoelectric material when under a DC bias field. From experiment, the coupling factor $k_{31}$ of this material is improved greatly and the highest value reached is 0.5. The data are shown in Figure 1-11, and the coupling factor increases with the DC bias field until it saturates. Compared with PVDF, the higher coupling factor makes this material a good candidate for energy harvesting. This will be discussed in Chapter 2.

It was also found that a bulky third monomer can be incorporated via the suspension polymerization process to convert the PVDF-TrFE from a normal ferroelectric to a relaxor ferroelectric polymer. This will be discussed in Chapter 4.
Figure 1-7: The temperature dependence of dielectric constant and dielectric loss data for PVDF-TrFE 65/35 after irradiation. The frequency is (from top to bottom for dielectric constant $K$ and from bottom to top for dielectric loss $D$) 100 Hz, 1 KHz, 10 KHz, 100 KHz, 1 MHz.

Figure 1-8: Comparison of the hysteresis loop between copolymer PVDF-TrFE and irradiated PVDF-TrFE. $P =$ charge density and $E =$ applied electric field.
Figure 1-9: Longitudinal strain of irradiated copolymer PVDF-TrFE at room temperature.

Figure 1-10: Transverse strain of the irradiated stretched PVDF-TrFE 68/32 copolymer.
1.2 The Single Crystal PMN-PT – High Electromechanical Coupling Factor and Large Strain Responses.

For the energy harvesting experiments using the electrostrictive polymer, DC bias and a complicated boundary control circuit is needed to achieve high efficiency. However, a DC bias field is not desirable for compact devices. As the next step, piezoelectric materials with the high electromechanical coupling factor and the large strain are investigated.

PMN as a typical relaxor ferroelectric material has been studied for many years. Smonlenskii et al. first derived the compositional heterogeneity model to understand the relaxor ferroelectric material. Cross further enhanced the understanding of the relaxor dielectric behavior and showed that the local polar nano-regions are similar to spin cluster behavior in super paramagnets, where the small ordering of spin clusters
establishes the inadequate magnetocrystalline anisotropy energy to remain stable against the thermal energy.\textsuperscript{16}

The most widely used relaxor is the PMN-PT solid solution system. The phase diagram of PMN-PT is shown in Figure 1-12.\textsuperscript{17} From the data, following the increase in PbTiO\textsubscript{3} (PT) content, the PMN-PT system slowly changes from a relaxor ferroelectric to a normal piezoelectric material. The morphotropic phase boundary (MPB) exists when the content of the PT is 33 %. At the same point, an anomalously high piezoelectric property is observed.\textsuperscript{28,29} From these results for the morphotropic phase boundary, the piezoelectric coefficients and coupling factor of PMN-PT are better than that of PZT. This creates many applications for this class of materials.

Moreover, PMN-PT and PZN-PT single crystals have been studied by many researchers. Recently it was reported that in relaxor ferroelectric single crystals of PZN-PT and PMN-PT a very high longitudinal electromechanical coupling factor (>0.9) can be achieved.\textsuperscript{23-24} Such a high coupling factor makes this material attractive for energy harvesting.

Zhang et al. investigated the parameters of single crystal PMN-33PT, including piezoelectric coefficient, elastic stiffness and coupling factor, which are shown in Table 1-3.\textsuperscript{25}
Figure 1-12: The phase diagram for the (1-x)Pb(Mb1/3Nb2/3)O3-xPbTiO3 solid solution system.17

Table 1-3: Measured and derived material properties of PMN–33PT multidomain single crystal poled in [001]25

<table>
<thead>
<tr>
<th>$c_{11}$</th>
<th>$c_{33}$</th>
<th>$c_{13}$</th>
<th>$c_{31}$</th>
<th>$c_{44}$</th>
<th>$c_{41}$</th>
<th>$c_{42}$</th>
<th>$c_{66}$</th>
<th>$c_{12}$</th>
<th>$c_{14}$</th>
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<tr>
<td>11.5</td>
<td>10.3</td>
<td>10.2</td>
<td>10.3</td>
<td>6.9</td>
<td>6.6</td>
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<td>0.05</td>
<td>0.15</td>
<td>0.15</td>
<td>0.35</td>
<td>0.5</td>
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Elastic compliance constants: $c_{ij} (10^{-12} \text{m}^2/\text{N})$

<table>
<thead>
<tr>
<th>$c_{11}$</th>
<th>$c_{22}$</th>
<th>$c_{33}$</th>
<th>$c_{44}$</th>
<th>$c_{55}$</th>
<th>$c_{66}$</th>
<th>$c_{12}$</th>
<th>$c_{14}$</th>
<th>$c_{15}$</th>
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<tbody>
<tr>
<td>69.0</td>
<td>-11.1</td>
<td>-55.7</td>
<td>119.6</td>
<td>14.5</td>
<td>15.2</td>
<td>44</td>
<td>-34</td>
<td>-4.1</td>
</tr>
<tr>
<td>±2.0</td>
<td>±1.2</td>
<td>±3.2</td>
<td>±4.0</td>
<td>±0.1</td>
<td>±0.2</td>
<td>±1.0</td>
<td>±1.0</td>
<td>±0.8</td>
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Piezoelectric constants: $d_i (10^{-11} \text{C/N})$

<table>
<thead>
<tr>
<th>$d_{31}$</th>
<th>$d_{33}$</th>
<th>$d_{15}$</th>
<th>$d_{13}$</th>
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<td>160</td>
<td>20.3</td>
<td>160</td>
<td>140</td>
<td>-1330</td>
<td>2820</td>
<td>10.3</td>
</tr>
<tr>
<td>±0.9</td>
<td>±1.6</td>
<td>±1.8</td>
<td>±10</td>
<td>±19</td>
<td>±75</td>
<td>±0.6</td>
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Dielectric constants: $\varepsilon (\varepsilon_0)$

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<th>$\varepsilon_{33}$</th>
<th>$\varepsilon_{13}$</th>
<th>$\varepsilon_{31}$</th>
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<tr>
<td>1434</td>
<td>680</td>
<td>1600</td>
<td>8200</td>
</tr>
<tr>
<td>±110</td>
<td>±45</td>
<td>±120</td>
<td>±200</td>
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</tbody>
</table>

Electromechanical coupling constants

<table>
<thead>
<tr>
<th>$\kappa_{11}$</th>
<th>$\kappa_{33}$</th>
<th>$\kappa_{13}$</th>
<th>$\kappa_{31}$</th>
<th>$\kappa_{15}$</th>
<th>$\kappa_{35}$</th>
<th>$\kappa_{13}$</th>
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<tr>
<td>0.32</td>
<td>0.59</td>
<td>0.04</td>
<td>0.44</td>
<td>0.77</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

$^a$Measure properties.
From the parameters in Table 1-3, single crystal PMN-PT at compositions near the MPB, when poled along the [001] direction, exhibits a very high electromechanical coupling factor ($k_{33} > 0.9$), which is extremely attractive for energy harvesting. However, single crystals pose some challenges, especially for reliability since single crystals are easy to fracture, and also because the growth is costly. In this thesis, I first investigate a 1-3 composite with PMN-PT single crystal in a polymer matrix. 1-3 composites in a polymer matrix reduce the elastic modulus which in turn improves the mechanical impedance match to the external mechanical environment. The polymer matrix also provides support to the single crystal PMN-PT, thereby improving the reliability, and reduces the cost, since polymer costs much less and is equally effective as long as the 1-3 composites can retain the high electromechanical coupling factor of the single crystal. In Chapter 2, we will develop and characterize 1-3 composites with PMN-PT single crystals. Furthermore, we will investigate energy harvesting using 1-3 composites and develop a resistor circuit to achieve a higher energy harvesting efficiency.

1.3 1-3 Composite

The conventional piezoelectric ceramic has the properties of relatively large electromechanical response, low cost and easy fabrication. It can be used for applications of piezoceramic in many areas. However, the high acoustic impedance of piezoceramics do not match well with the environment, and this mismatch lowers the energy efficiency of the acoustic wave during the transmission and reception.
Based on this, the composite structure has been investigated for the past several decades. In the late 1970's, Newnham et al. explored the concept of connectivity in the composite piezoelectric materials. Since then, the composites have found many applications in the engineering field, such as underwater acoustics, medical ultrasound, and wireless communications with high performance.

The composite can be fabricated by combining a piezoelectric ceramic or single crystal with a polymer or epoxy. It shows a greatly improved mechanical reliability, relatively high electromechanical response and low mechanical impedance. All these properties make it a better choice for many acoustic applications.

The concept of “connectivity” is introduced to categorize the PZT/epoxy composite. First, for a di-phasic composite, if one of the phases is connected in x, y, and z direction, it is labeled ‘3’. If a phase just connects in one direction, it is labeled as ‘1’. Similarly, if a phase does not connect in any x, y, z direction, it is labeled as ‘0’. Secondly, in most cases, a diphasic composite is labeled with a notation in m-n, where m indicates the connectivity of the first phase and n indicates the connectivity of the second phase. For example, a piezoceramic/polymer 1-3 composite means that the piezoceramic is just connected in one direction (Z direction, for example) and polymer is connected in all x, y, and z directions. There are 10 types of diphase composites: 0-0, …, 0-3, 1-1, …, 3-3, as shown in Figure 1-13.

Among these 10 types of composites, the 1-3 piezoceramic/polymer composite has become the most commonly used structure due to the large electromechanical response, improved mechanical reliability and lower mechanical impedance. In this thesis, I will investigate the properties of a 1-3 composite consisting of piezoelectric single crystal of
PMN-PT and polymer, including the dielectric constant, the piezoelectric coefficient, thickness mode coupling factor $k_t$ and the application of the composite to energy harvesting.

1.4 The Shape Memory Polymer

Shape memory materials are materials that recover their original shape under the stimulus of heating, magnetic field or light. These materials include shape memory alloy (SMA), shape memory ceramic (SMC) and shape memory polymer (SMP). Compared with other shape memory materials, SMP shows great advantages, such as low density, good moldability and low cost. Based on these excellent properties, a broad range of
applications have been developed using shape memory polymers, including medical devices, deployable aerospace structures, microsystems and auto-chokes for engine.\textsuperscript{38,39} In this thesis, SMPs are exploited for a novel class of hybrid SMP/EAP (electroactive polymer) actuators.

Shape memory polymer (SMP) was first developed by Mitsubishi Heavy Industries in Japan.\textsuperscript{39} In 1981, Ota et al. developed an SMP for application in heat-shrinkable tubing.\textsuperscript{38} Recently, many studies have been carried out for the biomedical application of SMP. Feninat et al. reviewed the biocompatibility concern and other issues of SMP for biomedical applications.\textsuperscript{41} Lendlein et al. also measured thermomechanical capabilities of SMP and discussed a biodegradable elastic shape memory polymer for biomedical applications.\textsuperscript{40} Furthermore, Lendlein et al. reported another type of shape memory polymer which is stimulated by light.\textsuperscript{42} It opens another broad new area for future applications. In addition, to exploit the application of SMP in MEMS, Gall et al. exploited the abilities of SMP for microfluidic reservoirs.\textsuperscript{36}

Figure 1-14 displays the fundamental temperature dependence of the elastic modulus of shape memory polymers. For shape memory polymers, the reduction in elastic modulus from the glassy state to the rubber state can be a factor of 200 over a narrow temperature range, which is a unique property of this class of polymers. Furthermore, the glass transition temperature of SMP can be modified within a wide range to adapt to various applications.\textsuperscript{39}
Figure 1-14: The temperature dependence of the elastic modulus change of SMP. 39

Figure 1-15: A schematic of the shape memory effect in SMPs, where $T_g$ is the glass transition temperature, $T_s$ is always less than $T_g$, $T_d$ can be above or below $T_g$, and $T_r$ is larger than $T_g$. 

$T_s =$ Storage Temperature
$T_d =$ Deformation Temperature
$T_r =$ Recovery Temperature
$T_g =$ Glass Transition
The working principles of SMPs are illustrated in Figure 1-15. There are four critical temperatures in this schematic diagram. $T_g$ is the glass transition temperature, where the material changes from the glassy state to the rubbery state. It is the reference point for thermo-mechanical deformation and recovery. $T_g$ can be adjusted within a broad range by modifying the synthesis process of shape memory polymer. $T_d$ is the deformation temperature, which can be below or above the glass transition temperature. However, if polymer is deformed below $T_g$ for a large strain level, the SMP ability can be permanently damaged. $T_s$ is below $T_d$ and the polymer exhibits a stable shape at that temperature. $T_r$ is always above $T_g$ and is the temperature where SMPs recover to the original shape. In this thesis, we will show that by combining an SMP with EAP, a novel class of hybrid actuator can be developed. This class of hybrid actuator makes use of the large elastic modulus change and shape memory effect of SMP with the active strain change in EAP to realize a hybrid actuator with extremely high elastic energy density and shape change capability.
References


30. S. Hayashi, “Polyurethane-Series Shape Memory Polymer”, Mitsubishi Heavy Industries, Ltd, Chapter 6


CHAPTER 2

ENERGY HARVESTING USING 1-3 SINGLE CRYSTAL PMN-33PT/EPOXY COMPOSITE

2.1 Introduction

In early studies of 1-3 composites, most research focused on the PZT/epoxy 1-3 composite, which is reliable and easily fabricated. Recently, it was reported that in relaxor ferroelectric single crystals of PZN-PT and PMN-PT, a very high longitudinal electromechanical coupling factor (>0.9) can be achieved.\textsuperscript{1,2} Such a high coupling factor is attractive for energy harvesting using electroactive materials. In this chapter, we investigate 1-3 composites with relaxor ferroelectric single crystal PMN-PT in a soft epoxy matrix for energy harvesting. The single crystal at the composition of 0.67PMN-0.33PT is chosen for this investigation. This composition is in the rhombohedra phase near the morphotropic phase boundary between the tetragonal and rhombohedra phases. When oriented and poled along the <001> direction, a piezoelectric $d_{33}$ coefficient higher than 2000 pC/N and a longitudinal coupling factor $k_{33}$ of 0.94 have been reported.\textsuperscript{3} However, the thickness coupling factor $k_t$ of the same crystals is not very high (in fact, it is nearly the same as that of the piezoelectric PZT ceramics).\textsuperscript{1,2} In this investigation, 1-3 single crystal/soft epoxy composites are employed to take advantage of the high $k_{33}$ coefficient and avoid the low $k_t$ of the single crystal. As has been shown both theoretically and experimentally for a properly designed 1-3 piezoceramic-polymer
composite, the thickness coupling factor can approach the longitudinal coupling factor of the piezoelectric phase.\textsuperscript{4 - 6} In addition, the soft polymer matrix also supports the fragile single crystals, improving the mechanical reliability while loading in energy harvesting experiments. The use of 1-3 composites also reduces the elastic impedance of the electroactive material system (defined as $\rho V_a$, where $\rho$ is the density and $V_a$ is the acoustic velocity). When harvesting energy from a person during walking or from other mechanical sources such as ocean waves, a lower mechanical impedance of the electroactive material system, compared with the piezoceramic and single crystals, is highly desirable.

2.1.1 Resonance Modes

First, we will discuss the constitutive equation of the piezoelectric material. From the definition of the piezoelectric material, those equations can be written as:

\begin{equation}
S = s^E T + dE \quad \text{Eq. 2.1}
\end{equation}

\begin{equation}
D = dT + \varepsilon^T E \quad \text{Eq. 2.2}
\end{equation}

where $s^E$ is the elastic compliance in short circuit, $d$ is the piezoelectric coefficient, and $\varepsilon^T$ is the dielectric constant under constant stress.\textsuperscript{14}

Rewriting Eq. 2.1 with stress and charge density as the independent variables gives

\begin{equation}
S = s^{\beta T} T + g, D \quad \text{Eq. 2.2}
\end{equation}

\begin{equation}
E = -gT + \beta^T D
\end{equation}
where \( g \) is the piezoelectric constant and \( \beta^S = \frac{1}{\varepsilon_{33}} \) is the dielectric permeabilities.

When strain and electric field are the independent variables we have:

\[
T = e^ES - e_iE
\]
\[
D = eS + e^S E
\]

Eq. 2.3

where \( e \) is the piezoelectric constant.

When strain and charge density are the independent variables Eq. 2.1 becomes:

\[
T = e^D S - h_i D
\]
\[
E = -hS + \beta^S D
\]

Eq. 2.4

where \( h_{33} \) is the piezoelectric constant and defined as \( h = (-\frac{\partial T}{\partial D})_S = (-\frac{\partial E}{\partial S})_D \).

Based on Eqs. 2.1 to 2.4, the piezoelectric constants are defined as: \(^7\)

\[
d = \left( \frac{\partial S}{\partial E} \right)_T = \left( \frac{\partial D}{\partial T} \right)_E
\]
\[
g = \left( \frac{-\partial E}{\partial T} \right)_D = \left( \frac{\partial S}{\partial D} \right)_T
\]
\[
e = \left( \frac{-\partial T}{\partial E} \right)_S = \left( \frac{\partial D}{\partial S} \right)_E
\]
\[
h = \left( \frac{-\partial T}{\partial D} \right)_S = \left( \frac{\partial E}{\partial S} \right)_D
\]

Eq. 2.5

Thus, the four piezoelectric constants have the following relations:

\[
d_{mi} = e^T_{nm} g_{ni} = e_{mj}^S \beta^E_{ji}
\]
\[
g_{mi} = \beta^T_{nm} d_{ni} = h_{mj}^D \beta^D_{ji}
\]
\[
e_{mi} = e^S_{nm} h_{ni} = d_{mj}^E \beta^E_{ji}
\]
\[
h_{mi} = \beta^S_{nm} e_{ni} = g_{mj}^E \beta^D_{ji}
\]

Eq. 2.6

However, the most important parameter of piezoelectric materials is the coupling factor. The coupling factor can be expressed as the ratio of the harvested electric energy \( W_1 \) to the input mechanical energy \( W_1 + W_2 \). Depending on the boundary condition, the
resonance mode can be separated into different modes, such as transverse mode, longitudinal mode, planar mode and thickness mode.

For the transverse mode, when the polarization direction is along the z direction and the stress is along x direction, a bar is free to cross-expand, so other stresses are zero, the static transverse coupling factor can be express as Eq. \ref{eq:2.7}: \[ k_{31} = \frac{d_{31}}{\sqrt{\varepsilon_{33}^{T} s_{11}^{T}}} \] Eq. 2.7

where \(d_{31}\) is the piezoelectric coefficient, \(\varepsilon_{33}^{T}\) is the dielectric constant in constant stress and \(s_{11}^{T}\) is the elastic compliance in short circuit condition.

When the conditions of one-dimension stress parallel to Z and polarization is also in the Z direction, the bar works in the longitudinal mode. In this case \(S_{1}=S_{2}\neq 0, S_{3}\neq 0, T_{1}=T_{2}=0, T_{3}\neq 0\), and the longitudinal coupling factor \(k_{33}\) can be expressed as:

\[ k_{33} = \frac{d_{33}}{\sqrt{\varepsilon_{33}^{T} s_{33}^{T}}} \] Eq. 2.8

The special case of one dimensional strain parallel to the polarization axis Z is called thickness mode. In this mode, the length and width of the sample are much larger than the thickness and \(S_{1}=S_{2}=0, S_{3}\neq 0, T_{1}=T_{2}\neq 0, T_{3}\neq 0\), so the thickness coupling factor can be expressed as:

\[ k_{t} = \frac{h_{33}}{\sqrt{c_{33}^{D} \rho_{33}^{S}}} = h_{33} \sqrt{\frac{\varepsilon_{33}^{S}}{c_{33}^{D}}} \] Eq. 2.9
where $h_{33}$ is the piezoelectric constant and defined as $h = (-\frac{\partial T}{\partial D})_S = (-\frac{\partial E}{\partial S})_D$, $e_{33}^D$ is the elastic stiffness, $\beta_{33}^\beta$ is the dielectric impermeabilities and defined as $\frac{1}{\varepsilon_{33}^S}$, and $\varepsilon_{33}^D$ is the dielectric constant.

For a planar resonance, the stress is planar isotropic perpendicular to $Z$ and polarization is in the $Z$ direction. In most cases, the sample is a round disk and the diameter of the sample is much larger than the thickness. We also have $T_1=T_2\neq0$, $T_3=0$; by symmetry, $S_1=S_2\neq0$, but generally $S_3\neq0$, so the coupling factor $k_p$ can be expressed as

$$k_p = \sqrt{\frac{2}{1-\sigma^E k_{31}}}$$

Eq. 2.10

where $\sigma^E = \frac{S_{12}^E}{S_{11}^E}$ is Poisson’s Ratio.

The boundary conditions of those resonance modes are shown in Figure 2-1. For a 1-3 composite, most of these materials work in the thickness mode. We will now derive the physical modeling of 1-3 composite piezoelectric in the thickness mode.
Figure 2-1: Resonance mode for piezoelectric material: (a) transverse mode (b) longitudinal mode (c) planar mode (d) thickness mode
2.1.2 The Physical Modeling of the 1-3 Composite

As discussed in Chapter 1, the 1-3 composite consists of the active material ceramic (or single crystal) and the inactive polymer material. Because the polymer phase is an isotropic homogeneous medium that is piezoelectrically inactive, the stress, strain and electrical displacement in the polymer phase of can be expressed as:

\[
\begin{align*}
T_i^p &= c_{11}^p S_i^p + c_{12}^p S_2^p + c_{12}^p S_3^p \\
T_j^p &= c_{12}^p S_i^p + c_{11}^p S_2^p + c_{12}^p S_3^p \\
T_k^p &= c_{12}^p S_i^p + c_{12}^p S_2^p + c_{11}^p S_3^p \\
T_4^p &= c_{44}^p S_4^p \\
T_5^p &= c_{44}^p S_5^p \\
T_6^p &= c_{44}^p S_6^p \\
D_i^p &= \varepsilon_{11}^p E_i^p \\
D_j^p &= \varepsilon_{11}^p E_j^p \\
D_k^p &= \varepsilon_{11}^p E_k^p \\
\end{align*}
\]

where the superscript p means the tensor is for the polymer phase.

In this chapter, we use piezoelectric ceramics as an example to investigate the constitutive equation of 1-3 composite. The ceramic is poled along the Z direction, and therefore the expressions for the ceramic phase are written:

\[
\begin{align*}
T_i^c &= c_{11}^c S_i^c + c_{12}^c S_2^c + c_{13}^c S_3^c - \varepsilon_{31}^c E_3^c \\
T_j^c &= c_{12}^c S_i^c + c_{13}^c S_2^c + c_{11}^c S_3^c - \varepsilon_{31}^c E_3^c \\
T_k^c &= c_{13}^c S_i^c + c_{12}^c S_2^c + c_{33}^c S_3^c - \varepsilon_{33}^c E_3^c \\
T_4^c &= c_{44}^c S_4^c - \varepsilon_{11}^c E_2^c \\
T_5^c &= c_{44}^c S_5^c - \varepsilon_{11}^c E_1^c \\
T_6^c &= c_{66}^c S_6^c \\
D_i^c &= \varepsilon_{15}^c S_i^c + \varepsilon_{31}^c E_1^c \\
D_j^c &= \varepsilon_{15}^c S_i^c + \varepsilon_{31}^c E_2^c \\
D_k^c &= \varepsilon_{15}^c S_i^c + \varepsilon_{31}^c S_2^c + \varepsilon_{33}^c S_3^c + \varepsilon_{33}^c E_3^c \\
\end{align*}
\]
where superscript c in the equation represents the ceramic phase. In both Eq. 2.11 and Eq. 2.12, the elastic stiffness and dielectric constant can be distinguished by the superscripts S and E, respectively. As our previous description, in the thickness mode the vibration is only in the Z direction, giving:

\[ E_1 = E_2 = 0 \]  

Eq. 2.13

In thickness mode, the sample is usually symmetric in the x-y plane, so we have:

\[ S_{11}^p = S_{11}^c, S_{12}^p = S_{12}^c \]  

Eq. 2.14

In the 1-3 composite, the polymer phase and the ceramic phase are intimately joined, so the strain in Z direction has the relation:

\[ S_{33}^p (Z) = S_{33}^c (Z) = \bar{S}_{33}(Z) \]  

Eq. 2.15

The electrode of polymer phase and ceramic phase are connected together, hence the electrical field should be the same in both of phase. This gives:

\[ E_{33}^p (Z) = E_{33}^c (Z) = \bar{E}_{33}(Z) \]  

Eq. 2.16

Then, the constitutive equations can be simplified by substituting Eqs. 2.13 to 2.16 into Eqs. 2.11 and 2.12. For the polymer phase, we have:\(^4\)

\[ T_{11}^p = (c_{11} + c_{12}) S_{11}^p + c_{12} \bar{S}_3 \]
\[ T_{33}^p = 2c_{12} S_{11}^p + c_{11} \bar{S}_3 \]  

Eq. 2.17
\[ D_{33}^p = \varepsilon_{11} E_3 \]

For ceramic phase, we have:
It can be assumed that the lateral stress $T_1$ in both the polymer phase and ceramic phase are the same. In a 1-3 composite, the ceramic is clamped by the polymer phase, so the lateral strain $S_1$ in ceramic phase should be compensated by the lateral strain in the polymer phase and the total strain of the composite in the lateral direction should be zero, giving:

$$T_1^p = T_1^c = T_1^t = 0$$

$$S_1^c = \frac{(c_{11}^p - c_{11}^c)S_3^c + e_{31}^c E_3}{\nu^p (c_{11} + c_{12}) + \nu^c (c_{11} + c_{12})}$$

$$S_1^p = \frac{(c_{11}^p - c_{11}^c)S_3^p + e_{31}^p E_3}{\nu^p (c_{11} + c_{12}) + \nu^p (c_{11} + c_{12})}$$

We substitute Eq. 2.20 into Eqs. 2.17 and 2.18 to replace the lateral strain $S_1$ of the polymer phase and the ceramic phase in the lateral stress equation:

$$
\overline{T}_1(Z) = \frac{c_{11}^c S_3^c}{c_{11}^c S_3^p} - e_{31}^c E_3
$$

where
For another stress \( T_3 \) and electric displacement \( D_3 \) in the Z direction of the polymer and ceramic phases results in: 4

\[
\begin{align*}
T_3 &= [c_{11} + \frac{2\nu \epsilon_{12} (c_1^E - c_{12})}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)}] S_3 - \frac{2\nu \epsilon_{12} c_{12}^E}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)} E_3 \\
D_3^p &= c_{11} E_3 \\
T_3^c &= [c_{33}^E - \frac{2\nu \epsilon_{12} (c_1^E - c_{12})}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)}] S_3 - \frac{2\nu \epsilon_{12} c_{12}^E}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)} E_3 \\
D_3^c &= [c_{33} + \frac{2\nu \epsilon_{12} (c_1^E - c_{12})}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)}] S_3 + \frac{2\nu \epsilon_{12} c_{12}^E}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)} E_3
\end{align*}
\]

Eq. 2.23

Since the ceramic post size is very small in the 1-3 composite, we assume that the effective total stress and the electric displacement are evenly distributed on the surface of the 1-3 composite. This giving:

\[
\begin{align*}
\bar{T}_3(Z) &= \nu' T_3^c(Z) + \nu'' T_3^p(Z) \\
\bar{D}_3(Z) &= \nu' D_3^c(Z) + \nu'' D_3^p(Z)
\end{align*}
\]

Eq. 2.24

Finally, the piezoelectric equation can be written as:

\[
\begin{align*}
\bar{T}_3 &= c_{33} \bar{S}_3 - \bar{e}_{33} \bar{E}_3 \\
\bar{D}_3 &= \bar{e}_{33} \bar{S}_3 + \bar{e}_{33} \bar{E}_3
\end{align*}
\]

Eq. 2.25

where

\[
\begin{align*}
-\epsilon_{33} &= \nu' [c_{33}^E - \frac{2
\nu \epsilon_{12} (c_1^E - c_{12})^2}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)}] + \nu'' c_{11} \\
-\epsilon_{33}^c &= \nu' [c_{33}^E - \frac{2
\nu \epsilon_{12} (c_1^E - c_{12})}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)}] \\
-\epsilon_{33}^c &= \nu' [c_{33}^E + \frac{2
\nu \epsilon_{12} (c_1^E - c_{12})}{\nu' (c_{11} + c_{12}) + \nu'' (c_{11}^E + c_{12}^E)}] + \nu'' e_{11}
\end{align*}
\]

Eq. 2.26
In summary, the constitutive equations for the 1-3 composite rederived to describe the material parameters of the 1-3 composite, such as elastic stiffness $c_{13}^E$ and $c_{33}^E$, piezoelectric constants $e_{33}$ and $e_{31}$, and dielectric constant $\varepsilon_{33}^S$. These constitutive equations are given by Eqs. 2.22 and 2.26.

2.2. 1-3 composite fabrication and characterization

Single crystals of 0.67PMN-0.33PT oriented along <001> direction are used in this investigation. The single crystals are poled at room temperature under a field of 10 kV/cm. The poled single crystals exhibit a $d_{33}$ of 2060 pC/N measured using a $d_{33}$ meter. In the 1-3 composite fabrication process, extra precaution must to be taken not to damage the single crystals. The poled single crystals of 1 mm thick (<001> oriented) are first diced along the <100> direction using the Automatic Dicing Saw K&S 982-6 (supplied by Kulicke & Soffa Industries) to a width of 100 $\mu$m, then diced in the perpendicular direction to produce an array of posts with a rectangular cross section (see Figure 2-2(a)).

The dimensions (0.1 and 0.3 mm along the two perpendicular directions) of the single crystal rods are much smaller than the thickness of the crystal (or length of the rods along the z-direction, see Figure 2-2(b)), which is required in order to realize the longitudinal coupling factor of the crystal in the composite. The cutting process is followed by filling with Mereco 1650 series epoxy to form a 1-3 composite (see Figure 2-2(a)). The Young’s modulus of the epoxy is 14 MPa, much smaller than that of single crystal. The 1-3 composites are polished to a thickness of about 0.7 mm and sputtered Au films of 20
nm thick are used as the electrodes. The finished composites are poled again along the thickness direction in silicon oil for 5 min under a DC field of 10 kV/cm. This second poling process is necessary to create a large piezoelectric coefficient and large electromechanical coupling factor of the composites.

The dielectric, piezoelectric, and electromechanical properties were characterized for the 1-3 composites. For a 1-3 composite, since the two constituents are electrically in parallel (Figure 2-2 (b)), from Eq. 2.26 the dielectric constant can be expressed as

\[ \varepsilon_{33} = \varepsilon_v \varepsilon_3 + \frac{2\varepsilon_p (\varepsilon_{31})^2}{\varepsilon_v (c_{11} + c_{12}) + \varepsilon_p (c_{11}^E + c_{12}^E)} \varepsilon_p \]  

Eq. 2.27

In this equation, from Table 1-4 for single crystal PMN-33PT in Chapter 1, the piezoelectric constant \( e_{31} \) is -3.9 C/m² and the elastic stiffness \( c_{11}^E \) and \( c_{12}^E \) are approximately \( 11 \times 10^{10} \) N/m², which are much larger than the value of the elastic stiffness \( c_{11} \) of the epoxy (14 MPa). Thus, the second term in Eq. 2.27 can be neglected. The equation for the dielectric constant simplifies to:

\[ \varepsilon_{33} = \varepsilon_v \varepsilon_3 + \varepsilon_p \]  

Eq. 2.28

Figure 2-3 presents data for the dielectric constant as a function of temperature (measured during cooling) for a 1-3 single crystal composite with 44.4 % volume fraction of PMN-PT single crystal. For comparison, the data for the single crystal of the same composition and orientation is shown in Figure 2-3(b). The dielectric peak at 130°C for the composite is the same as that in the single crystal. At room temperature, the dielectric constant of the crystal is 3390 and the 1-3 composite is 1536, which is close to 44.4 % of
3390 (=1505). The result indicates that the 1-3 composite fabrication process used in this investigation does not have a marked effect on the single crystal piezoelectric properties.

Figure 2-2: (a) Optical image of 1-3 composite, dark area: PMN-33PT, white area: Epoxy; (b) Diphase 1-3 composite arranged in parallel configuration along the z-direction (hatched area, PMN-PT and white area, epoxy).
For 1-3 composites with a small aspect ratio (the width of the crystal rods and width of the polymer phase curf vs the thickness), the piezoelectric coefficient $d_{33}$ of 1-3 composites can be expressed as:  

$$d_{33} = \frac{\nu_1 d_{33}^2 s_{33} + \nu_2 d_{33} s_{33}^2}{\nu_1 s_{33}^2 + \nu_2 s_{33}^2}$$  

Eq. 2.29

where $d_{33}$ and $d_{33}^2$ are the piezoelectric coefficient and $s_{33}$ and $s_{33}^2$ are the elastic compliance of phase 1 and phase 2, respectively. For the PMN-PT/Epoxy composite, the piezoelectric coefficient of the epoxy $d_{33}$ is 0 and the elastic compliance of epoxy $s_{33}$ is much larger than $s_{33}$ ($7.1 \times 10^{-8} >> 1.2 \times 10^{-10}$), which yield $d_{33} \approx 1d_{33}$. Direct measurement of the $d_{33}$ coefficient of 1-3 composites using a $d_{33}$ meter shows that this is indeed the case.

As has been shown by many earlier works on piezoelectric 1-3 composites, the thickness electromechanical coupling factor $k_t$ of 1-3 composites, which is the coefficient related to the energy harvesting experiment in this paper, can be very close to the longitudinal coupling factor $k_{33}$ of the single crystal.  

The coupling factor $k_t$ of the 1-3 composites is characterized using an HP Impedance Analyzer (HP Model 4284A) and the data is shown in Figure 2-4. From the series resonance frequency $f_s$ and the parallel resonance frequency $f_p$, $k_t$ can be determined from  

$$k_t^2 = \frac{\pi f_s}{2 f_p} \tan(\frac{\pi f_p - f_s}{2 f_p})$$  

Eq. 2.30
Figure 2-3: The dielectric constant as a function of temperature for (a) 1-3 PMN-33PT/Epoxy composite with a 44.4% volume fraction of PMN-PT and (b) PMN-33PT single crystal (measured at cooling @ 1 kHz)
The coupling factors of composites with different volume fraction of PMN-PT single crystals are shown in Figure 2-5. For the composition with the fraction of PMN-PT single crystals near 50 %, the coupling factor $k_t$ reaches 0.855, close to the single crystal $k_{33}$ value of about 0.9. This is higher than the values reported by other group’s earlier result on single crystal-polymer composite.

This difference might be due to the polymer matrix since the matrix used here possesses a very low elastic modulus. For the comparison, the coupling factor $k_t$ of the single crystal is also measured and it is 0.59.

The elastic stiffness $c_{33}^{D}$ of the 1-3 composite can be deduced from the resonance frequency\textsuperscript{12}

$$c_{33}^{D} = \rho (2t \rho_f)^2$$ \hspace{1cm} Eq. 2.31

where $\rho$ is the density of the composite and $t$ is its thickness. Using

$$c_{33}^{E} = (1 - k_t^2) c_{33}^{D}$$ \hspace{1cm} Eq. 2.32

the elastic stiffness under constant electric field can also be obtained. The elastic stiffness $c_{33}^{D}$ and $c_{33}^{E}$ as a function of the volume fraction of PMN-PT single crystals are shown in Figure 2-6: both $c_{33}^{E}$ and $c_{33}^{D}$ increase with the volume fraction of the single crystal and the elastic stiffness of 1-3 composites with about 50 % of single crystals is much smaller than that of the crystal, which is the expected result.
Figure 2-4: Electrical impedance $Z$ and phase angle $\theta$ for a PMN-33PT/Epoxy composite with 0.56 volume fraction, thickness/width = 1.7

Figure 2-5: Thickness coupling coefficient $k_t$ vs. volume fraction for PMN-33PT/Epoxy composites, open circles, experimental data and solid curve, a fitting to the data.
Figure 2-6: (a) Elastic stiffness constant $c_{33}$ vs. volume fraction and (b) elastic compliance constant $c_{33}^e$ vs. volume fractions for 1-3 PMN-33PT/Epoxy composite. Data points are shown and solid curves are drawn to guide eyes.
As a comparison, 1-3 composites of piezoceramic PZT in a polymer matrix are also used in the energy harvesting experiment. The 1-3 piezocomposites are purchased from Smart Material Corp. The volume fraction of the PZT ceramic is 40 %. The electric impedance curve for the PZT-piezoceramic/polymer composite is shown in Figure 2-7. The coupling factor deduced from the resonance data is 62.8 %. The elastic stiffnesses $c_{33}^E$ and $c_{33}^D$ of the PZT composite are $3.32 \times 10^{10}$ N/m² and $2.1 \times 10^{10}$ N/m², respectively.

Figure 2-7: Electrical impedance $Z$ and phase angle $\theta$ for a PZT/Epoxy composite with 0.4 volume fraction.
2.3 Energy Harvesting using 1-3 composites

Using electroactive materials to parasitically harvest electric energy from various mechanical sources is attractive for a broad range of applications, especially in view of the fact that some of these materials can be made into flexible forms and in very small volumes. In a typical energy harvesting process, an electroactive material absorbs the external mechanical energy, and through a proper electromechanical conversion process converts that energy into electric form. Finally, this converted electric power, through a power electronic interface, is delivered to the electronic load. Therefore, several steps must be taken in designing an energy harvesting system to effectively convert the mechanical energy available in an external medium into the electric energy to be delivered to an electric load: (i) a mechanical impedance match of the electroactive material system to the environment to realize maximum mechanical energy transfer into the electroactive material system; (ii) high electromechanical conversion efficiency of the electroactive material system; and (iii) proper power electronics to efficiently transfer converted electric power into the electric load. Here we focus on the electroactive material system, which includes possible modification to the pure material by other mechanical or electrical parts. These additions or modifications may improve the electromechanical conversion efficiency and/or the mechanical impedance match to the external mechanical environment.\(^{15-16}\)

The schematic of the energy harvesting experiment set-up is shown in Figure 2-8, where the harvested electric energy is delivered to a resistive load. In the experiment, a Universal Test Machine (MTS 810, supplied by Material Test System Corp) is employed
to provide the mechanical energy input to the electroactive materials (an AC compressive stress of 4 to 10 Hz). The compressive stress is applied along the poling direction (the 3- or z-direction). The energy harvesting experiment is also intended to evaluate how high of a stress field can be applied to the composites to generate a high electric energy density output without damaging and stress depoling the composite. For PMN-PT single crystals, it has been shown that a very large strain can be induced by an external applied electric field for the crystals at the composition investigated here when oriented along the <001> direction.1-2

Figure 2-8: Schematic for the energy harvesting experiment set-up in this study.

Hence, it is expected that in poled composites, a high stress can be applied to induce large strain and consequently a large mechanical energy density in the composites. It has also been shown by several earlier investigations that a high compressive mechanical stress applied to a piezoelectric material, as in the energy harvesting experiment presented here, can depole the piezoelectric material.17 In order to prevent possible depoling at high stress level, a DC electric bias field is applied to the composites.
to stabilize the polarization against high compressive stress. A very large resistor \( R_1 \) is used to isolate the DC power source from the AC energy harvesting circuit (the \( R_1C_s \) time constant is much larger than \( 1/f \) where \( f \) is the AC mechanical signal frequency, in the 4 to 10 Hz range in the present experiment, and \( C_s \) is the capacitance of the electroactive composites).

For the piezo-composites in the energy harvesting experiment, assuming that the non-zero strain component is \( S_3 \) (the strain \( S \) along the applied stress direction due to the fact that the lateral dimensions are much larger than the thickness of the composites), which is close to the experimental situation, the piezoelectric constitutive relations are:

\[
T = c^E S - e E \\
D = e S + \varepsilon^s E
\]

where \( c^E \) is the elastic stiffness under constant field, \( e \) is the piezoelectric constant, \( \varepsilon^s \) is the dielectric permittivity under constant stress, \( T \) is the stress component \( T_3 \), \( E \) is the electric field \( E_3 \) and \( D \) is the displacement component (\( D_3 \)).

The sinusoidal mechanical force \( F = F e^{i\alpha} \) applied to the sample generates a sinusoidal voltage and strain according to:

\[
F e^{i\alpha} = \bar{c}^E l_0 e^{i(\omega t + \alpha)} - \bar{e} \nu_0 e^{i(\omega t + \theta)} \\
Q = \bar{d} l_0 e^{i(\omega t + \alpha)} + C_0 V e^{i(\omega t + \theta)}
\]

Eq. 2.34
where $A$ is the cross section and $t_0$ is the thickness, $l_0 = St_0$ is the displacement, $F = TA$ is the applied force, $Q = DA$ is the charge, $V = Et_0$ is the voltage, $\bar{\varepsilon} = e \frac{A}{t_0}$, $\bar{\varepsilon} = e \frac{A}{t_0}$, and

$$C_0 = \frac{\varepsilon \sigma A}{t_0},$$

respectively.

The current generated in an external load is therefore:

$$I = \frac{\partial Q}{\partial t} = i \omega e l_0 e^{i(\omega t + \alpha)} + i \omega C_0 V_0 e^{i(\omega t + \theta)}$$

Eq. 2.35

and the generated voltage is given by:

$$V_0 e^{i\theta} = RI = R[i \omega e l_0 e^{i\alpha} + i \omega C_0 V_0 e^{i\theta}]$$

Eq. 2.36

where $R$ is the total external load resistor ($R_4$ in our experiment). Solving these equations yields the generated voltage:

$$V_0 e^{i\theta} = \frac{i R \omega e l_0 e^{i\alpha}}{1 - i \omega RC_0}$$

Eq. 2.37

and the power dissipation in the load resistor is

$$Power = \frac{V_0^2}{2R} = \frac{R e^2 l_0^2 \omega^2}{2(1 + \omega^2 R^2 C_0^2)}$$

Eq. 2.38

Eq. 2.38 shows that when the load resistor is equal to the impedance of the sample voltage source, the maximum power dissipated in the resistor can be reached, i.e., when

$$R = \frac{1}{\omega C_0}$$

Eq. 2.39
the peak power is

\[ \text{Power}_{\text{peak}} = \frac{\varepsilon^2 l_0^2 \omega}{4C_0} \]  \hspace{1cm} \text{Eq. 2.40} \\

or the power density is \( \frac{\varepsilon^2 S^2 \omega}{4\varepsilon^3} \). Eq. 2.40 shows that the output power is proportional to the excitation frequency of the mechanical force, the square of the displacement and the piezoelectric constant of the material. This means if a high strain and high piezoelectric constant material are used that the harvested electric energy would improve greatly. For the single crystal PMN-33PT, the strain can be more than 1 %, which is much larger than the strain of the piezoceramic. ¹

The relationship between the output power and input mechanical \( F \) can also be derived. From Eqs. 2.34 and 2.37, \( l_0 \) is:

\[ l_0 e^{i\alpha} = \frac{F}{\varepsilon^2} \frac{iR \omega \varepsilon^2}{1 - i\omega RC_0} \]  \hspace{1cm} \text{Eq. 2.41} \\

In addition,

\[ \frac{\varepsilon^2}{\varepsilon'^2} = 1 + \frac{\varepsilon^2}{\varepsilon'^2 C_0} \]  \hspace{1cm} \text{Eq. 2.42} \\

Substituting Eqs. 2.41 and 2.42 into Eq. 2.38 yields the harvested power in the load resistor

\[ \text{Power} = \frac{\text{Re}^2 \omega^2 F^2}{2(\varepsilon^2)} [1 + (\omega RC_0)^2 \left( \frac{1}{1-k_i^2} \right)^2] \]  \hspace{1cm} \text{Eq. 2.43} \\

Hence, the maximum power delivered to the load resistor is achieved when
and the maximum power in this case is given by:

$$R = \frac{1 - k_i^2}{\omega C_0}$$

or the peak power density is

$$\frac{T^2 k_i^2 \omega}{4c^k}$$

The result indicates that the output power density is proportional to the square of the stress, the excitation frequency of the mechanical force, and the coupling factor of the material. It is also inversely proportional to the elastic stiffness of the material. Hence, a soft material with high electromechanical coupling factor will deliver higher output electrical energy. The 1-3 composites with PMN-PT single crystals meet these conditions.

It should be pointed out that the equations derived are based on the assumption that all the coefficients do not change with the applied mechanical stress and electric field.

The schematic of the energy harvesting experiment using a resistor load is shown in Figure 2-8. The energy harvested is measured directly from the voltage across $R_2$. In the experiment, two different types of 1-3 composites are used. One is the 1-3 PMN-33PT/epoxy composite. Another one is PZT/epoxy 1-3 composite, which is used for comparison.

To determine the maximum output power under a constant stress, a variable resistor is connected to the circuit and a 88.9 MPa AC stress (4 Hz) is applied to the 1-3 composite (56 % of PMN-PT crystal). The result is shown in Figure 2-9 and the maximum power density is 96 mW/cc when the load resistor is 9.5 Mohm. Under high
compressive stress, both the capacitance and the coupling factor will decrease compared with their stress-free values and hence the load resistor value at high stress for the maximum power output is higher than that at stress free case (~4 MPa). Such a non-linear material response is a common feature of piezomaterials. In this experiment, a DC bias field of 4.65 kV/cm is applied to prevent the stress depoling. After energy harvesting, the coupling factor \( k_t \) of the 1-3 composite is measured and the results show that the coupling factor of the composite does not change after the energy harvesting cycle, indicating that no depoling occurs under a high stress level when the composites are subject to the DC bias field.

For the comparison, the dependence of the power harvested on the stress is measured using 1-3 PZT/epoxy composite. As shown in the data of Figure 2-10(a), when no DC bias is applied to the composites, a partial depolarization occurs which results in a much smaller harvested power as the stress amplitude is reduced (reduction of the coupling factor and piezoelectric coefficient). When a high DC bias field is applied, shown in Figure 2-10(b), the harvested energy is enhanced because the DC bias prevents the partial depoling of the 1-3 composite during the measurement. The maximum power density is 12 mW/cc from 1-3 PZT/epoxy composite under a 40 MPa AC stress of 4 Hz.
The results from these studies are summarized in Table 2-1. Due to higher coupling factor, the harvested energy density of 1-3 composite with single crystal (22.1 mW/cc under 40.4 MPa) is almost 2 times that harvested with the PZT ceramic 1-3 composite (12 mW/cm$^3$ under 39 MPa).

At higher stress levels, the harvested energy density of 1-3 PMN-PT single crystal composite can be 96 mW/cc, which corresponds to an energy density of 24.1 mJ/cc. From Table 2-1, when the applied mechanical stress is increased by $88.9/40.4 \approx 2.2$ times, the square dependence of the output power on the applied stress indicates that the harvested energy density should be increased by 4.8 times. The result in Table 2-1 shows an increase in the power density of $(96.2/22.1) 4.4$ times, close to 4.8 as predicted.

Figure 2-9: Harvested power density verse the load resistor in the circuit for the 1-3 PMN-PT/Epoxy composite with volume fraction 56.3%. Applied AC stress amplitude is 88.9 MPa, DC bias field is 4.35 kV/cm, and the sample dimension is 10 mmx10 mmx0.69 mm.
It should be pointed out that because the composites are insulators, there is very little energy consumption of the DC power source used to provide DC bias voltage. In fact, such a DC voltage source can be provided by the harvested electric energy through properly designed power electronics.

Table 2-1: Summary of the experimental results

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume Fraction</th>
<th>( c_{33}^{D} / c_{33}^{E} ) (GPa)</th>
<th>Stress (MPa)</th>
<th>Power Density (mW/cc)</th>
<th>Energy Density (mJ/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3PZT/Epoxy composite</td>
<td>40%</td>
<td>34.8/21</td>
<td>39</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>1-3 Single Crystal PMN-33PT/</td>
<td>37.5%</td>
<td>49/12.8</td>
<td>40.4</td>
<td>22.1</td>
<td>5.53</td>
</tr>
<tr>
<td>Epoxy composite</td>
<td>56%</td>
<td>60/15.6</td>
<td>88.9</td>
<td>96.2</td>
<td>24.1</td>
</tr>
</tbody>
</table>
Figure 2-10: Harvested power density vs applied mechanical stress for a PZT/Epoxy composite with 0.4 volume fraction. Sample diameter: 2 cm diameter and thickness: 1.1 mm. (a) DC bias = 0V and (b) DC bias=5.45 kV/cm. The direction of the stress cycle is indicated in the figure.
2.4. Conclusions

In this chapter, the theoretical modeling for 1-3 composite is derived and the Mason equivalent circuit of the thickness mode resonance is also discussed. Furthermore, 1-3 PMN-PT single-crystal/polymer composites are investigated for energy harvesting applications. To make use of the high strain capability and hence the high energy density while maintaining mechanical integrity, 1-3 composites are a preferred form for the single crystals to be utilized for energy harvesting. The single crystal PMN-PT/epoxy composites with different volume fraction of single crystals are fabricated and characterized. The results show that for a properly designed and fabricated 1-3 single crystal/polymer composite, the thickness coupling factor $k_t$, which is used in this energy harvesting experiment, can be very close to the longitudinal coupling factor $k_{33}$ of the single crystal.

In the energy harvesting experiments, a resistive load circuit is used to measure the energy harvested. Based on the piezoelectric constitutive equations, the relations between the input mechanical strain, stress and harvested electrical energy density are derived. For comparison, energy harvesting using 1-3 PZT/epoxy composites is also performed. Due to the higher coupling factor, the harvested energy density from 1-3 PMN-PT/epoxy composite is about 2 times higher than that from the 1-3 PZT/epoxy. Under a mechanical stress of 88.9 MPa at 4 Hz, a harvested energy density of near 0.1 W/cc can be achieved. The experimental results also show that a high stress (more than 40 MPa) can be applied to 1-3 single crystal composites without damaging the composites and a DC bias field applied to the composites is very effective at preventing
stress depoling in the composites. No degradation is observed after many energy harvesting cycles under high stress using these 1-3 composites.
References:


CHAPTER 3

ENERGY HARVESTING USING AN ELECTROSTRICTIVE POLYMER

3.1 Introduction

Harvesting energy from ambient environments is an emerging technology attractive for many applications ranging from portable electric devices to renewable energy. The best candidates for converting mechanical energy to electric energy are electroactive materials such as piezoelectric and electrostrictive materials for many energy harvesting applications.1-4

In nature, there are many sources that can be utilized to harvest energy, such as solar energy, wind power, water flow, the mechanical motion of people, and others. In most of the applications, due to the much higher energy density of piezoceramics and piezoelectric polymers as compared with electrostatic or electromagnetic devices, these materials were utilized to harvest electrical energy.1,5 Previous researchers have claimed that the footfall of a person’s heel through 5 cm can generate 67 W of power.6 This makes it possible to use smart materials and specially designed circuits to harvest the electrical energy of people walking.

In 1992, Schmidt investigated harvesting electrical power from the wind by using PVDF mounted in the windmill.5 Kymissis invented a shoe to use the piezoelectric ceramic and PVDF to harvest energy from people walking. They estimated that a 10 mW energy harvesting system that lasts for 2 years is equivalent to a 150 cm$^3$ lithium-thionyl
chloride battery. It means that energy harvesting is feasible to replace batteries in the small systems.

However, in all these earlier works, no effort has been devoted to actively tune the electrical boundary condition in the energy harvesting process, which has the potential to realize large improvements in system performance. In this chapter, we will discuss how to control the electrical boundary condition to achieve higher efficiency in the energy harvesting process.

For this investigation, low frequency energy harvesting processes, such as people walking and ocean wave energy are considered. However, the concept can be easily extended to high frequency harvesting systems (at the resonance condition). A general form of the system is illustrated in Figure 3-1.

From this figure, it is clear that there are several key requirements for the energy harvesting system.

1. Good material impedance matching with the environment.
2. High coupling factor of material
3. Improvements in system efficiency are possible through smart electronics to reach levels much higher than that of the material alone.

To facilitate the discussion, we will briefly introduce the constitutive equation for the piezoelectric and electrostrictive materials.
3.2 The Electrostrictive Polymer PVDF-TrFE

Since the 1990’s, the electrostrictive polymers have attracted a great deal of attention due to the high energy density, easy processing, relatively high electromechanical response and broad applications.\(^7-^9\) Due to the high energy density, this class of material is very attractive in performing the energy conversion between the electric and mechanical energy forms. Under a DC bias, this material can also be treated as a piezoelectric material. Relative to the conventional piezoelectric PVDF-TrFE, it has a much higher piezoelectric coefficient and coupling factor.\(^10\) These properties make this material attractive for harvesting electrical energy from the environment.

In most of earlier investigations, the piezoelectric ceramics were utilized in the energy harvesting mode,\(^11-^12\) where a stress (T) is applied to a piezoelectric material and a charge (D) will be generated. This is called the direct piezoelectric effect. On the other hand, when an electric field (E) is applied to the material, a strain will be generated in this material. This is called converse piezoelectric effect.

Figure 3-1: A general form of the energy harvesting cycle.
When the linear elastic (Hooke’s law) and dielectric relations are included, the full tensor form of the piezoelectric constitutive relation can be written as Eq. 3.1:

\[
S_{ij} = d_{ij}E_k + s_{ijkl}T_{kl}
\]
\[
D_j = \varepsilon_{ik}^E E_k + d_{ik}^T T_{ij}
\]

where \(d_{ij}\) and \(d_j\) are the piezoelectric coefficient, \(s_{ijkl}\) is the elastic compliance, \(\varepsilon_{ik}^E\) is the dielectric permittivity, and \(i, j, k, l = 1, 2, 3\). In the equation, the convention in which repeated indices are summed is used. The superscripts \(E\) and \(T\) refer to the condition under which these quantities are measured. That is, compliance is measured under a constant electric field (short circuit condition) and dielectric constant is measured under a constant stress. Due to the electromechanical coupling in a piezoelectric material, the elastic compliance under a constant electric field can be very different from that under constant charge.

For the electrostrictive polymer, strain has a quadratic dependence on the polarization:

\[
S = QP^2
\]

where \(Q\) is the charge related electrostrictive coefficient and \(P\) is polarization of the ferroelectric material.

To the linear dielectric material, the polarization is related to the dielectric constant by

\[
P = (\varepsilon - \varepsilon_0)E
\]

where \(\varepsilon_0\) is the dielectric permittivity in the vacuum. Finally, the Eq. 3.3 becomes
Similarly with Eq. 3.1, if the linear elastic (Hooke’s law) and dielectric relations are considered, the full tensor form of the piezoelectric equation can be written as:

\begin{align*}
S_y &= M_{\eta k}E_k E_j + s^{\eta}_{\eta k}T_{kl} \\
D_i &= \varepsilon_{i k}^T E_k + 2M_{\eta k}E_i T_{kl}
\end{align*}  

Eq. 3.5

An isotropic electrostrictive polymer film contracts along the thickness direction and expands along the film direction when an electric field is applied across the thickness, assuming that the only nonzero stress is that applied along the length of the film. The constitutive relation then is simplified to:

\begin{align*}
S &= sT + ME^2 \\
D &= \varepsilon E + 2MET
\end{align*}  

Eq. 3.6

where:

\begin{align*}
E &= E_3, D = D_3, S = S_3 \\
T &= T_3, s = s_{31}, M = M_{31}, \\
\varepsilon &= \varepsilon_{33}
\end{align*}  

Eq. 3.7

Because our analysis is based on these simplified relations, the subscripts and superscripts of these parameters and field variables are omitted in the following.

### 3.3 Energy Harvesting Cycle and Effect of Boundary Conditions

Presented in Figure 3-2 is a typical energy harvesting cycle used in many publications to illustrate the energy conversion process in a piezoelectric material. In this energy harvesting cycle, the total input mechanical energy density from the external
mechanical source to the piezoelectric material is $W_1 + W_2$ and the harvested electric energy density is $W_1$. The coupling factor or the energy conversion efficiency, therefore, is

$$\frac{W_1}{W_1 + W_2} = k^2$$  \hspace{1cm} \text{Eq. 3.8}

Eq. 3.8 illustrates two important factors for an energy harvesting system. In order to achieve high electric energy output from a mechanical source, a high coupling factor of the electromechanical material is required and a high mechanical energy density in the material is also highly desirable (large $W_1 + W_2$). In this chapter, we will investigate one of these materials, the electrostrictive PVDF based polymers, for energy harvesting. We will also examine how various external electrical and mechanical conditions influence the energy harvesting process with the electrostrictive polymer, especially the output electric energy density and energy conversion efficiency.

In general, in an energy harvesting cycle for an electrostrictive material, both the mechanical variables, i.e., the stress $T$ and strain $S$, and the electrical variables, i.e., the electric field $E$ and electric displacement $D$, will vary as illustrated in Figure 2-1. In both the mechanical and electrical planes the material state traverses a closed loop. In the mechanical plane the rotation is counter-clockwise, while in the electrical plane the rotation is clockwise. This rotation designates that the net energy flow is from mechanical to electrical. The area enclosed in the loop of the mechanical and electrical planes is equal, and is the converted energy density. By controlling the imposed electrical conditions, we can vary the area of the energy cycle so that $W_1$ and $k^2$ can be optimized for different experimental environments.
Figure 3-2: The mechanical cycle for energy harvesting systems using piezoelectric materials.

Figure 3-3: Energy harvesting cycle for the electrostrictive material.
3.3.1 Energy Harvesting Cycle 1: Constant field and Open Circuit Boundary Condition

The standard energy harvesting process for a piezoelectric material is shown in Figure 3-2. When the stress is increased from zero to the maximum (T\text{max}) condition, it is at the short circuit condition. When the stress is from the T\text{max} to zero, it is open circuit condition. During this process, the elastic compliance $s_{33}^E$ and $s_{33}^O$ vary depending on these variable boundary conditions. The enclosed area is the harvested electrical energy $W_1$. For an electrostrictive material, the situation is different. In energy harvesting using an electrostrictive polymer, the DC bias is necessary to keep the material from becoming a piezoelectric material. The stress dependence strain circle of the electrostrictive material is shown in Figure 3-4. At first, in condition 1, before the stress is applied on the sample, the sample is under DC bias $E_0$. From condition 1 to 2, it is in the constant
electrical field $E_0$ (short circuit). When the stress $T$ is in the maximum stress $T_{\text{max}}$, then from 2 to 3, it is in the open circuit condition. Due to the electrostrictive property of the material, this route under open circuit is not a straight line, as shown in Figure 3-4. From condition 3 to 1, the generated charge is released and the electrical field applied on the material is returned to $E_0$. This is a standard energy harvesting circle for an electrostrictive material.

The total input mechanical energy is $W_1 + W_2 = \frac{1}{2} s T_{\text{max}}^2$ and the harvested electrical energy $W_1$ can be calculated from the electric field $E$ and electric displacement $D$ circle.

From the electric cycle of Figure 3-4, because stress $T$ is zero in condition 1 and from Eq. 3.5, the electrical displacement is given by

$$D_1 = \varepsilon E_0$$  \hspace{1cm} \text{Eq. 3.9}

As the material is at condition 2, the stress $T$ is in the maximum $T_{\text{max}}$. The electrical displacement can be expressed as:

$$D_2 = \varepsilon E_0 + 2 M E_0 T_{\text{max}}$$  \hspace{1cm} \text{Eq. 3.10}

As the material is in the open-circuit condition from state 2 to 3, the electric displacement is constant. Thereby $D$ in the condition 3 can be expressed as:

$$D_3 = \varepsilon E_3 = \varepsilon E_0 + 2 M E_{\text{max}}$$  \hspace{1cm} \text{Eq. 3.11}

The electric field in condition 3 is given by:

$$E_3 = E_0 \left(1 + \frac{2 M T_{\text{max}}}{\varepsilon}\right)$$  \hspace{1cm} \text{Eq. 3.12}
We define a parameter $\gamma$ by:

$$\gamma = \frac{2MT_{\text{max}}}{\varepsilon} \quad \text{Eq. 3.13}$$

The harvested electrical energy $W_1$ can be expressed as:

$$W_1 = \frac{1}{2}(E_3 - E_0)(D_2 - D_1) = \frac{2M^2T_{\text{max}}^2E_0^2}{\varepsilon} \quad \text{Eq. 3.14}$$

Therefore, the coupling factor is given by:

$$k^2 = \frac{w_1}{w_1 + w_2} = \frac{2M^2T_{\text{max}}^2E_0^2}{\varepsilon} \cdot \frac{1}{\frac{1}{2}sT_{\text{max}}^2} = \frac{4M^2E_0^2}{s\varepsilon} \quad \text{Eq. 3.15}$$

If $E_0$ is chosen a certain value, the maximum electrical field can be achieved at condition 3, which is expressed as:

$$E_{\text{max}} = (1 + \gamma)E_0 \quad \text{Eq. 3.16}$$

If we substitute this equation into the expression for $W_1$, the maximum coupling factor can be expressed as:

$$k^2 = \frac{4M^2E_0^2}{s\varepsilon} = \frac{4M^2E_{\text{max}}^2}{(1 + \gamma)^2s\varepsilon} \quad \text{Eq. 3.17}$$
3.3.2 Energy harvesting cycle 2- sinusoidal applied electric field during the stress-strain cycle

In this section we analyze the case where the mechanical and electrical excitations consist of constant components and sinusoidal-varying components of the same frequency, as shown in Figure 3-5.

$$E_3 = E_{ac} \sin(\omega t) + E_b$$
$$T_1 = T_{ac} \sin(\omega t + \phi) + T_b$$  \hspace{1cm} \text{Eq. 3.18}$$

where $\omega$ is the angular frequency, $E_3$ is the electric field added to the EAP film, $T_1$ is the stress used to stretch the EAP film to generate the electric energy, $E_{ac}$ is the AC voltage and $E_b$ is the DC bias voltage. Because the sample is pre-stretched, $T_b$ is non-zero in Eq. 3.18.

A phase difference $\phi$ exists between the sinusoidal component of the electric field and mechanical excitation. We substitute $E$ in Eq. 3.18 into the electrical displacement $D$
in Eq. 3.6, and current density is derived from the derivative of the electric displacement with respect to time:

\[ i = \omega E_{ac} \cos(\omega t) + 2\omega M (E_{ac} T_{ac} \sin(2\omega t + \phi) + E_{ac} T_{ac} \cos(\omega t) + E_{ac} T_{ac} \cos(\omega t + \phi)) \]  

Eq. 3.19

The electrical field \( E_3 \) in Eq. 3.18 is multiplied by current \( i \) in Eq. 3.19 to calculate the harvested energy density \( W_1 \). Because the integration of the sinusoidal function in one period is zero, the only component in Eq. 3.19 contributing to the electrical power is \( E_{ac} T_{ac} \cos(\omega t + \phi) \). It can be shown that the harvested energy density for one period of the sinusoidal excitation is given by

\[ W_1 = \int_0^T i Edt = 2 \pi M E_{ac} E_{ac} T_{ac} \sin \phi \]  

Eq. 3.20

where \( W_1 > 0 \) corresponds to a positive net energy flow from the active material to the electronic circuit while \( W_1 < 0 \) is for the case when the electric energy flows from the electronics to the active material, in which the active material works as an actuator. It can be seen that when \( \phi = 90 \), \( W_1 \) reaches maximum.

The harvested energy density will be maximized when \( E_{ac} = E_{ac} = \frac{1}{2} E_{max} \), \( T_{ac} = \frac{1}{2} T_{max} \) and \( \phi = -\pi / 2 \). The energy density under these conditions is therefore:

\[ W_{1max} = \frac{\pi}{4} M E_{max}^2 T_{max} \]  

Eq. 3.21
3.3.3 Comparison of two energy harvesting cycles

As an example, the material properties of the electrostrictive copolymer PVDF-TrFE is used as input parameters for a comparison of the two energy harvesting cycles analyzed in the preceding sections. The maximum electric field and stress value are within the safe operating range. The parameters of electrostrictive P(VDF-TrFE) are listed in Table 3-1, where $M$ is the electrostrictive coefficient.

Table 3-1: Parameters of the electrostrictive PVDF-TrFE copolymer.

<table>
<thead>
<tr>
<th>Electrostrictive Material</th>
<th>$\varepsilon_{33}$</th>
<th>$M$</th>
<th>$s_{11} (Pa^{-1})$</th>
<th>$E_{\text{max}}$ (MV/m)</th>
<th>$T_{\text{max}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiated copolymer PVDF-TrFE</td>
<td>$45 \varepsilon_0$</td>
<td>$2 \times 10^{-18}$</td>
<td>$1 \times 10^{-9}$</td>
<td>150</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 3-2: Maximum energy density harvested and coupling factor for the two energy harvesting cycles for the electrostrictive PVDF-TrFE copolymer

<table>
<thead>
<tr>
<th>Electrical Conditions</th>
<th>$W_{1\text{max}}$ (J/cm³)</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant field and open-circuit</td>
<td>0.117</td>
<td>0.483</td>
</tr>
<tr>
<td>AC Excitation</td>
<td>0.706</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3-2 shows that for the electroactive polymer, even for the same properties, using an AC excitation condition allows the harvesting of much more energy that possible for standard energy harvesting method, such as the constant field and open circuit. In addition, the sinusoidal excitation condition is convenient to control. Therefore, the sinusoidal excitation condition is selected to improve the efficiency of energy harvesting.
3.4 Energy Harvesting Using Electroactive Polymer and Experiment Setup

As introduced in Chapter 1, the irradiated copolymer PVDF-TrFE shows a very high electrostrictive strain (>5%) and a high elastic energy density $U_m (>0.5 \text{ J/cm}^3)$. Such a high electromechanical response makes this class of polymer attractive for active energy harvesting applications.

In the following, we will examine the output electric energy density and energy conversion efficiency using the electrostrictive PVDF in the active energy harvesting mode while under AC excitation.

3.4.1 The experimental setup

As a first step, a setup was developed which can measure the Young’s Modulus, the strain of the polymer film, the piezoelectric coefficient $d_{31}$ and the coupling factor $k_{31}$. The setup is situated on a micopositioner, which can accurately adjust the position of the loudspeaker and loadcell. The mechanical driver of the energy harvesting system consists of a loudspeaker (6Ω, Aiwa) driven by an audio amplifier (PM175, Carver). The stress in the EAP is measured by a load cell (ELPM-T3E-1KL, Entran Device Inc). A Fotonic sensor (MTI 2000, MTI Instruments) measures the transverse strain of the sample. The setup diagram is shown schematically in Figure 3-6.

Using the transverse strain and the stress from load cell, the Young’s modulus can be determined by:

$$Y = \frac{\text{Stress}}{\text{strain}} \frac{T_1}{S_i}$$  \hspace{1cm} \text{Eq. 3.22}
The Young’s modulus of the irradiated copolymer PVDF-TrFE samples were measured at room temperature. A comparison of the data from the setup in Figure 3-6 and the data from Dynamic Mechanical Analysis (DMA) are shown in Figure 3-7(a) and Figure 3-7(b), respectively. It is found that the data is consistent at 1 Hz, meaning that the designed setup can successfully measure the Young’s modulus of the thin film at room temperature.

Figure 3-6: The schematic of the mechanical setup used for the Young’s modulus measurement.
Figure 3-7: (a) The Young’s modulus using the designed setup at 1 Hz and 
(b) the temperature dependence of the Young’s modulus of irradiated copolymer PVDF-TrFE at 1 Hz.
Based on the setup in Figure 3-6, we designed a Labview control program was
designed to vary the boundary condition and concomitantly measure the harvested energy
instantaneously. Figure 3-8 shows a schematic of the whole energy harvesting setup. The
electrical boundary condition is controlled by the voltage supply (Model 610D, Trek Inc)
through Labview program, which controls the mechanical and electrical excitation of the
whole system using the signal conditioning system (SC-2345, National instruments) of
the computer.

During the experiment, the designed Labview program controls the input signal of
the loudspeaker to generate the required force and strain in the film. Meanwhile, the
output signal of the loadcell and Fotonic sensor are fed into this program to calculate the
stress and strain data of the film. From Eq. 3.18, the sinusoidal excitation boundary
condition needs the AC and DC voltages to optimize the energy output, which can be
realized by the voltage supply (Trek 610) through the same program. Meanwhile, the
generated voltage and current signals from the polymer sample are read by the Labview
program to calculate the harvested energy in the experiment. Since the DC bias is
blocked by the polymer capacitor and integration of AC field during one period is zero,
the integrated output power in one period then is the net harvested energy. In this setup,
the amplitude and phase of the AC voltage can be adjusted to optimize the energy
conversion efficiency.
Figure 3-8: (a) Schematic drawing of the experimental system for the energy harvesting and (b) the pictures of the energy harvesting system.
3.4.2 The energy loss during energy harvesting

To provide reliable electrodes for the EAP film during the energy harvesting cycle in which the film experiences large strain change (~4%), a thin polypyrrole conducting polymer electrode is deposited on both sides of the EAP film before evaporation of Al. 20-21 Afterwards, 20 nm Al is evaporated on both surfaces of the EAP film to enhance the conductivity of the conducting polymer electrode. A DC bias field is applied to the electrostrictive PVDF film to establish an effective piezoelectric state.

In the experiment, it was found that the energy loss in a dielectric material is a critical factor affecting the energy conversion efficiency of the system. In the designed Labview system, when the energy measured in the system is positive, it means that energy is consumed and there is energy loss in the system. When the phase difference between the mechanical force and AC field is adjusted, the energy loss can be maximized. Figure 3-9 shows the AC voltage dependence of energy loss during the energy harvesting experiment under various DC electric fields and frequencies. It was observed that the energy loss increases with AC field. It was also found that the energy loss depends not only on the magnitude of the AC electrical field, but also the frequency of AC electrical field and DC bias field. At the same frequency and AC electrical field, the energy loss decreases with the DC bias. These energy losses come from the dielectric losses of the electrostrictive material due to polarization hysteresis.
3.4.3 The harvested energy

The electrical signal and mechanical force in Eq. 3.18 are applied to the polymer sample, which is held between the load cell and loudspeaker in the setup shown in Figure 3-8. The output energy is calculated by the Labview program automatically. The AC electrical field phase dependence of output energy is shown in Figure 3-10.

During the experiment, the different electrical fields and the phases are varied to optimize the electrical boundary condition. It is found that in certain phases, the specific energy can be negative, which means that an electric energy is harvested. This result is consistent with Eq. 3.20. On the other hand, a positive energy in Figure 3-10 corresponds to the energy consumed during the experiment.
From the data in Figure 3-9, the energy loss decreases with DC bias field. Therefore in the experiment, a high DC bias field and low AC excitation electrical field maximizes the harvested energy. It is found that when the phase difference between the AC force and AC electrical field is negative, an electric energy can be harvested. The data shows that for $E_{DC}=46.1\text{MV/m}$, $E_{AC}=21\text{MV/m}$ and the phase angle difference is about $-90^\circ$ (Figure 3-11(a)), the harvested power can be 91.3 $\mu\text{W}$ at 1 Hz (Figure 3-11(b)). This corresponds to a harvested electric energy density of 39.4 mJ/cm$^3$, where the polymer film dimension is 23.04mm x 7.72mm x 13μm.

Figure 3-10: The electrical field phase dependence of the specific energy density.
Figure 3-11 (a) Recorded AC voltage and force signal on the electrostrictive polymer versus time and (b) the power spectrum of the harvested electric power when $\phi=\pi/2$. 
The stress-strain cycle of this energy harvesting process is shown in Figure 3-12, which is similar to the sinusoidal excitation curve shown in Figure 3-5. A strain of about 3 % is induced in the energy harvesting cycle. The enclosed area, as explained earlier, is the harvested electrical energy.

The AC electrical field–electrical displacement circle is shown in Figure 3-13. This cycle is in the clock-wise direction, indicating that the net energy flow is from the polymer film to the electrical circuit. Therefore, electric energy is harvested.

![Figure 3-12: The recorded strain-stress curve in the energy harvesting cycle with the electrostrictive polymer and active energy harvesting scheme.](image)
From the data in Figure 3-12, the efficiency as defined in Eq. 3.8 is estimated to be about 10%. For a comparison, using Eq. 3.6, Eq. 3.18 and the experimental values of $E_b=46.1\text{MV/m}$, $E_{ac}=21\text{MV/m}$, $T_{ac}=T_b=T_{max}=12.5\text{MPa}$, $s_{11}=1 \times 10^{-9}$ and $\phi=\pi/2$, as well as the parameters in Table 3-1, the theoretical derived stress-strain cycle is shown in Figure 3-14. This strain-stress cycle can be compared with experiment result shown in Figure 3-12.

Furthermore, in Figure 3-14, the area enclosed in the cycle is the harvested energy $W_1$ while the area under the cycle is $W_2$. The total input mechanical energy is $W_1+W_2$. After the integration of the enclosed area, the total input mechanical energy density is about $0.37\ \text{J/cm}^3$. The harvested energy density $W_1$ is about $0.15\ \text{J/cm}^3$. This is an ideal situation. The energy conversion efficiency could reach 40%, which is much higher than the experimental efficiency. This discrepancy is caused by several factors such as the
elastic loss and dielectric loss which reduce the electric energy output. Furthermore, for active materials under high strain and fields, it is well known that the response behavior will deviate from that in Eq. 3.5 and Eq. 3.6. The non-linear dielectric response of the relaxor ferroelectric polymer also causes the strain-field relationship to deviate from that in Eq. 3.4.

Figure 3-14: The simulated strain-stress cycle using the parameters in the energy harvesting experiment.

Additionally, in all the energy harvesting systems, there is electric energy consumed by electronics. For the active energy harvesting system investigated here, no direct measurement on the electric energy consumed was performed. Based on the measurement results for other energy harvesting systems with similar electronics, the efficiency of the power electronics is at 93.5 %. Using this value, it can be estimated that the electric energy consumed is about 17 mJ/cm², which reduces the net electric energy output to
22.4 mJ/cm³. This energy consumption can be reduced substantially if much more electroactive polymers are used in the energy harvesting system.

Table 3-3 shows the experiment results reported in the literature using the piezopolymers and piezoceramics with the conventional energy harvesting scheme, in which the efficiency is below 5 % and the harvested electric energy density is below 5 mJ/cm³. 1,26-27 This table also shows the experiment results in Chapter 2 using 1-3 PZT/Epoxy and 1-3 single crystal PMN-33PT/Epoxy composite. As compared with all those results, the harvested energy density from the electrostrictive polymer PVDF-TrFE represents a marked improvement and demonstrates the potential of active energy harvesting in achieving higher efficiency, which coupled with the high elastic energy density of the electrostrictive polymers yields a much higher electric energy harvested.

Table 3-3: Comparisons of several energy harvesting materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Conversion Efficiency (%)</th>
<th>Harvested Energy Density (mJ/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferroelectric PVDF¹</td>
<td>0.5</td>
<td>0.044</td>
</tr>
<tr>
<td>PZT¹</td>
<td>1.5–5</td>
<td>2.1</td>
</tr>
<tr>
<td>1-3 PZT/Epoxy composite</td>
<td>N/A</td>
<td>3</td>
</tr>
<tr>
<td>1-3 single crystal PMN-PT/Epoxy composite</td>
<td>N/A</td>
<td>24.1</td>
</tr>
<tr>
<td>Electrostrictive PVDF-TrFE</td>
<td>10</td>
<td>39.4</td>
</tr>
</tbody>
</table>
3.5 Summary

In this chapter, we discussed methods to modify the boundary conditions, including constant-field and open-circuit and the sinusoidal applied electric field boundary conditions in the framework of the active energy harvesting process. Furthermore, based on the high efficiency and easy implementation of the sinusoidal excitation boundary conditions an energy harvesting system was build to realize this boundary condition using the electrostrictive polymer PVDF-TrFE. The dielectric loss and elastic loss of polymer material reduce the harvested energy and efficiency. However, it was found the harvested energy density and energy conversion efficiency of this material are still much higher than those of the piezoelectric PVDF and ceramics.
References:


CHAPTER 4

A COMPACT ELECTROACTIVE POLYMER ACTUATOR SUITABLE FOR
REFRESHABLE BRAILLE DISPLAY

4.1 Introduction

The irradiated copolymer exhibits a strain level of 5 % and elastic energy density of greater than 1 J/cm³, which are much higher than the properties of the piezoelectric polymer PVDF-TrFE. However, the irradiation process also induces unwanted side effects in the polymer. Furthermore, some defects are not permanent and can be erased when the films are heated to a temperature near or above the melting temperature. Compared with irradiation, direct chemical modification is more attractive, where the copolymer is synthesized with a third monomer in which the 3rd monomer acts as a defect. Such third monomers that have been broadly studied include chlorotrifluoroethylene (CTFE) and chlorofluoroethylene (CFE).

Recently, P(VDF-TrFE-CFE) was synthesized by suspension polymerization with an oxygen-activated initiator. Based on the experimental results, the terpolymer shows a large strain, slim hysteresis loop and large elastic energy density (~1 J/cc). Relative to the irradiated copolymer, the terpolymer eliminates the undesirable drawbacks from irradiation, such as the non-uniform film quality, the formation of the crosslink and chain scission.

Several compositions of the terpolymer have been investigated in the last several
years. By properly designing the composition of the terpolymer, the all *Trans* conformation can be effectively eliminated and *Trans-Gauche* conformation of terpolymer is increased. The polymer material as a whole is changed from the ferroelectric phase to the relaxor ferroelectric phase. Figure 4-1 and Figure 4-2 show the polarization loop and dielectric properties of the terpolymer. Both of them exhibit properties of typical relaxor ferroelectrics, such as a reduced hysteresis loop and maximum dielectric constant ($T_m$) shifting progressively towards higher temperatures with frequency. Based on early investigations, the third monomer CFE is partial included in the structure of the PVDF-TrFE and acts as a defect, similar to the defect introduced by irradiation.

For convenience, the composition of the terpolymer is labeled as $\text{PVDF}_x\text{-TrFE}_{(1-x)-\text{CFE}_y}$, where the real mole ratio of VDF and TrFE can be calculated by the ratio of $x$ and $1-x$ to $1+y$. Based on the properties of the terpolymer as an actuator, in this thesis the investigated terpolymer composition is 70/30/8.1.
Figure 4-1: The hysteresis loop of terpolymer PVDF-TrFE-CFE (70/30/8.1) at room temperature.

Figure 4-2: The temperature dependence of the dielectric constant and dielectric loss of the terpolymer. The frequencies are (from top to bottom for dielectric constant $k$ and from bottom to top for dielectric loss $D$) 100 Hz, 1 KHz, 10 KHz, 100 KHz, 1 MHz.
4.2 Characterization of the PVDF-TrFE-CFE Terpolymer

Various methods are used to characterize the properties of the PVDF-TrFE-CFE terpolymer, such as Differential Scan Calorimetry (DSC), Wide Angle X-ray Diffraction (WAXD), Fourier Transformer Infrared Spectroscopy (FTIR), longitudinal strain and transverse strain measurement.

4.2.1 DSC Measurement

Differential Scanning Calorimetry (DSC) is one of the Thermal Analysis (TA) technologies used to detect of the thermal properties of the material. Essentially, DSC is utilized to measure the ferroelectric-paraelectric transition temperature, the glass transition temperature, the crystalline melting enthalpy and the melting temperature.

In this analysis, the DSC scans were performed at a heating rate of 10°C/min in a TA Instruments Q100, with 20 ml/min N₂ flow rate. All the samples were solution-cast polymer film.

The comparison of DSC data for PVDF-TrFE (75/25) and PVDF-TrFE-CFE terpolymer is shown in Figure 4-3. It is visible that for the terpolymer, the ferroelectric-paraelectric phase transition peak around 116°C in PVDF-TrFE copolymer is eliminated. This means that the terpolymer PVDF-TrFE-CFE is changed to a relaxor ferroelectric material. Furthermore, other research results also support that the defect in terpolymer by the third monomer lead the reducing of the domain size and change the polymer to a relaxor ferroelectric material.⁸
The melting enthalpy ($\Delta H_m$) and the melting temperature are related to the crystallinity and lamellae thickness, respectively. From the data in Figure 4-3, the melting enthalpy $\Delta H_m$ (32.3 J/g) in PVDF-TrFE (75/25) copolymer is much higher than the $\Delta H_m$ of the terpolymer (16.7 J/g), which means that there is a much lower crystallinity in the terpolymer as compared with PVDF-TrFE copolymer.

4.2.2 Wide Angle X-ray Diffraction Analysis

X-ray diffraction is a non-destructive method to detect the crystallinity, lamellae size and chemical composition of material. According Bragg’s law, diffraction occurs when the incident wavelength is same as the interatomic length. This effect is dependent on the incident angle of the X-ray beam, so the diffraction pattern gives diffraction intensity as a function of the scattering angle.

Figure 4-3: DSC data of the copolymer PVDF-TrFE (75/25) and PVDF-TrFE-CFE (70/30/8.1).
In this chapter, X-ray data were collected in the 200/110 peak range by a Scintag Cu-Kα diffractometer with wavelength 1.5454 Å. From Chapter 1, the PVDF-based polymer is a semi-crystalline material, which means the crystal phase is embedded in the amorphous phase. The X-ray data of PVDF-TrFE-CFE terpolymer consist of the superposition of the crystalline peak with an amorphous halo. The crystallinity of the material should be the ratio of the crystalline peak area to the total peak area. Figure 4-4 shows the 200/110 peak fitting of the terpolymer PVDF-TrFE-CFE. There are two fitted peaks under the real diffraction peak, where the solid line and the dashed line indicate the crystalline peak and of the amorphous halo, respectively.

Furthermore, to reveal the crystal structure of the terpolymer, the X-ray data of the terpolymer is compared with copolymer PVDF-TrFE 75/25 and shown in Figure 4-5. In this figure, the peak around 20 degrees for PVDF-TrFE (75/25) represents the polar phase and the peak around 18 degree for the terpolymer PVDF-TrFE-CFE represents the non-polar phase. It is evident that the terpolymer has no polar phase.
Figure 4-4: The 200/110 peak fitting of the X-ray data of the terpolymer PVDF-TrFE-CFE (Solid line: the crystalline peak; Dash line: Amorphous halo).

Figure 4-5: X-ray data for the terpolymer and copolymer PVDF-TrFE (75/25) in the 200/110 peak range. (Dashed line: PVDF-TrFE 75/25; solid line: terpolymer.)
4.2.3 FTIR Characterization

Fourier Transform Infrared (FTIR) Spectroscopy is another way to characterize the crystal structure of the material. When infrared light interacts with a material, it results in molecular vibration depending on the bond energetics. The chemical structure fragment (functional group) within molecules tends to absorb infrared at certain wavelengths. This means that there is a relation between the wavelength and the material structure, making FTIR a useful method to detect the crystal structure of the material.

In this chapter, the FTIR data are mainly used to monitor the change to chain conformation, specifically the all-Trans (peak at 1285 cm$^{-1}$), the $T_3G_3G'$ (peak at 510 cm$^{-1}$) and $TGTG'$ (peak at 610 cm$^{-1}$) when going from the PVDF-TrFE copolymer to the PVDF-TrFE-CFE terpolymer. The fraction $F_i$ of each conformation can be calculated by the following equation:

$$F_i = \frac{A_i}{A_i + A_{II} + A_{III}}$$  \hspace{1cm} \text{Eq. 4.1}

where $A_i$ is the fitting peak area of a particular chain conformation ($i = I, II, III$). $A_I$, $A_{II}$, $A_{III}$ are the fitting peak areas of the chain conformation of all Trans, $T_3G$ and $TG$, respectively.

Figure 4-27 shows the FTIR data of the copolymer PVDF-TrFE and terpolymer PVDF-TrFE-CFE. It reveals that the all Trans conformation (1280 cm$^{-1}$) disappears in terpolymer. Even the $T_3G_3G'$ conformation in the terpolymer is much reduced in amplitude. The TG conformation, however, is considerably increased in the terpolymer. This means that the third monomer adds defects to the copolymer chain and changes the
conformation from the polar phase (all *Trans*) to non-polar phase (*TGTG*'). All these results are consistent with our DSC and WAXD measurement results.

**4.2.4 Longitudinal Strain and Young’s Modulus Measurement**

The longitudinal strain of the terpolymer 70/30/8.1 was measured by photonic sensor. The strain setup was given previously.\(^8\) The data in Figure 4-7 indicate that the strain of the terpolymer is much larger than the conventional PVDF-TrFE copolymer. Even compared to the irradiated copolymer, the strain of the terpolymer is still improved, which means the third monomer is successfully synthesized into the polymer chain and the terpolymer can be used to replace the irradiated copolymer and fabricate devices.
Dynamic mechanical analysis (DMA) was performed with a TA DMA 2980 instrument in the step-scan and tensile mode with frequencies from 0.1 to 20 Hz. Samples for DMA are relatively thick (~100 µm). From the data in Figure 4-8, the Young’s modulus of terpolymer (70/30/8.1) is about 200 MPa, which is about 5 times smaller than the conventional PVDF-TrFE copolymer. However, the strain of the terpolymer is increased to more than 50 times relative to the piezoelectric material PVDF. The elastic energy density can be expressed as

\[ E = \frac{1}{2} Y S^2 \]  

Eq. 4.2

where \( Y \) is the Young’s Modulus and \( S \) is the strain. From Eq. 4.2, the total elastic energy density of the terpolymer is improved many times from the ferroelectric polymer PVDF.

Based on the high strain and the high elastic energy density, the terpolymer becomes a preferred material to fabricate the actuator devices. The full-page Braille display is one of these devices.
Figure 4-7: The longitudinal strain of the PVDF-TrFE-CFE (70/30/8.1) terpolymer. The sample was prepared by the solution cast method and annealed at 120 °C for 5 hours.

Figure 4-8: The temperature dependence of the Young’s modulus of the terpolymer (70/30/8.1) at 10 Hz.
4.3 Market Demand for a Full-Page Refreshable Braille Display

Solid state actuators with large strain and high elastic energy density are attractive for a broad range of applications. One area where these actuators will have great impact is the refreshable Braille display, where piezoelectric ceramic actuators are currently used. Due to the small transverse strain level of the piezoceramics (< 0.05%), the actuator is in the bimorph configuration to “amplify” the actuation to reach required Braille dot displacement (>0.5 mm), as schematically shown in Figure 4-9(a), which results in a large Braille cell size (see Figure 4-9(b)). The bulky size and fragility of the piezoceramic bimorph actuator and high cost of each actuator for the refreshable Braille display limit the development of a practical full page refreshable Braille display and graphic display.

To circumvent this difficulty associated with the piezoceramic bimorph actuators, several alternative actuation methods have been investigated, such as the pneumatic and thermopneumatic actuators, to realize a full page refreshable Braille display with size, weight, and cost acceptable to the user community. However, various shortcomings associated with these new technologies prevent them from being practical for the full page display. In 2000, a wheel-based Braille display was reported which can significantly reduce the number of actuators to move the dots in a refreshable display and hence, can reduce the cost of the Braille display markedly. However, the moving wheel display appears to not to be accepted by the user community.

The high performance of the electroactive terpolymer provides an opportunity to develop compact Braille actuators, which can directly replace the bulky piezoceramic
bimorph actuators, as schematically shown in Figure 4-10, for refreshable full page Braille display with compact size and much reduced cost.

In this chapter, we investigate the issues related to the electrostrictive polymers for a compact actuator, with the performance and size suitable for the full page Braille display. We examine various conductive polymers for the EAP film electrodes and developed a screen printing method, based on a unique conductive polymer, to deposit the patterned conductive polymer electrode to the terpolymer film surface with strong bonding and minimal thickness, which can also easily scaled up to mass production. We also investigated self-healing of these EAP films after an electric breakdown. In mass production of EAP actuator films, it is inevitable that the films contain weak spots, causing electric breakdown. It was found that the thin conductive polymer electrodes, due to the low melting point and the polymer chemistry, can lead to self-healing and this requires less electrical energy to burn out the breakdown spot relative to aluminum electrodes. In this investigation, EAP films were wound on a thin spring to form compact Braille actuators. For the standard Braille display, the dot displacement and dot spacing are 0.025 inch (0.635 mm) and 0.1 inch (2.54 mm), respectively. There are 32 or 20 cells with 8 dots per cell in the commercial product. Results to be presented in this paper indicate that the actuator performance exceeds the requirements for the Braille actuator.

In the following, the experimental details of the electroded terpolymer films will be presented. Then, the results related to the self-healing, which are crucial for reliable operation, will be discussed, followed by the Braille actuator fabrication and characteristics. The key points related to the EAP Braille actuator will be summarized at the end.
Figure 4-9: (a) Schematic of a bimorph actuator and (b) schematic of the commercial Braille cell using piezoelectric bimorph.

Figure 4-10: Schematic of the proposed EAP Braille cell using the compact EAP Braille actuators.
4.4 The electrode clamping effect on the EAP strain response

For electroactive polymer films with large strain (> several % strain), metal electrodes as used in piezoceramic and piezopolymers pose several problems. First, the metal electrodes have a short lifetime due to fracture under high strain. In addition, the high elastic modulus of the metal electrodes will also impose mechanical constraint to the active polymers, which will reduce the strain level of the active polymer. In the past, we have developed several methods for depositing conductive polymer electrode layer on EAP films. However, these early methods either take too long to deposit electrodes, unsuitable for mass production of EAP actuators, or produce electrode layers that do not form strong bonds with the EAP film surface. In this chapter, several conductive polymers as well as their deposition methods are investigated. It was found that a PEDOT Baytron S V2 conducting polymer (Bayer Corporation), which is an aqueous dispersion of poly(3, 4-ethylendioxythiophene)-poly(styrenesulfonate), can be easily screen printed or sprayed on the surface of P(VDF-TrFE-CFE) terpolymer with strong bonding. No surface treatment of the terpolymer film is needed and the electrode layer can be very thin (~0.1 µm). In order to produce thin polymer film electrodes with different thickness, the commercial Baytron S V2 can be diluted by ethyl alcohol. The electrode pattern on the screen printer was fabricated using a photolithography method. The electroded terpolymer films are nearly transparent as shown in Figure 4-11 due to the thinness of the conductive polymer layers.
Figure 4-11: An image of the terpolymer film coated by a thin layer of conductive polymer. The conductive polymer layers (both top and bottom electrodes) are nearly transparent so the text underneath the polymer films is visible.

Figure 4-12: The transverse strain of P(VDF-TrFE-CFE) film (6 µm thick) using conducting polymer electrode. Circles indicate an electrode thickness of 2 µm, and triangles 0.1 µm.
The transverse strain of the electroded terpolymer films along the stretching direction was characterized by a photonic sensor.\textsuperscript{20,21} The data for the terpolymer films (8 $\mu$m film thickness) with 0.1 $\mu$m thick conductive polymer electrode layer are shown in Figure 4-12. The transverse strain is 3.5 % under 100 MV/m, which is similar to what has been measured earlier on thick films (for >25 $\mu$m thickness).\textsuperscript{7,8} For such an EAP films to generate 1 mm Braille dot displacement, the actuator length is $\sim$3 cm (see Figure 4-10).

During the experiment, it was found that the electrode thickness has a critical effect in the strain of the terpolymer. As also shown in Figure 4-12, the electromechanical strain becomes very small when the conductive polymer layer thickness is 2 $\mu$m, comparable to that of the terpolymer film. Since the elastic modulus of the conductive polymer (>1 GPa) is higher than that of the terpolymer (~0.5 GPa), and thin terpolymer films are required in order to reduce the applied voltage, the electrode clamping effect must be considered in the design of the EAP Braille actuators. In the following, the mechanical clamping effect of the electrode layer on the strain response of the terpolymer films is examined.

If there is no external mechanical stress under an applied field $E$, the terpolymer film displays intrinsic transverse electrostrictive strains $S_{10}$ and $S_{20}$, along and perpendicular to the film stretching direction, respectively (see Figure 4-9(a)). Due to the electrode layer clamping effect, the strains will be reduced to $S_1$ and $S_2$:

\[
S_1 = S_{10} + s_{11}T_1^p + s_{12}T_2^p
\]
\[
S_2 = S_{20} + s_{22}T_2^p + s_{12}T_1^p
\]

\textbf{Eq. 4.3}
where $s_{11}$ and $s_{22}$ are the elastic compliances of the EAP along and perpendicular to the stretching direction, respectively. $T_{1}^p$ and $T_{2}^p$ are the clamping stresses to the polymer film due to the electrode layers.

The transverse strains $S_{1}^m$ and $S_{2}^m$ in the electrode layer should be the same as $S_{1}$ and $S_{2}$ and the elastic equations for the strains in the electrode layer are:

$$S_{1}^m = s_{11}^m T_{1}^m + s_{12}^m T_{2}^m$$
$$S_{2}^m = s_{22}^m T_{2}^m + s_{12}^m T_{1}^m$$

where $s_{11}^m$ and $s_{22}^m$ are the elastic compliances of the electrode layer. $T_{1}^m$ and $T_{2}^m$ are the stresses exerted to the electrode layer from the polymer film.

Because the clamping force to the polymer film and the stretching force to the electrode layer should be equal in magnitude with opposite sign, it can be derived that:

$$\frac{T_{1}^m}{T_{1}^p} = \frac{T_{2}^m}{T_{2}^p} = -\frac{t_p}{t_m} = -A$$

Eq. 4.5

where $t_m$ and $t_p$ are the total thickness of the electrode layers and the polymer layer, respectively. $A$ is the thickness ratio between the polymer and electrode layers. Substituting $T_{1}^p$ and $T_{2}^p$ for $T_{1}^m$ and $T_{2}^m$ into Eq. 4.4, and for the electrode layer $s_{11}^m = s_{22}^m$ yields:

$$S_{1}^m = -s_{11}^m T_{1}^p A - s_{12}^m T_{2}^p A$$
$$S_{2}^m = -s_{11}^m T_{2}^p A - s_{12}^m T_{1}^p A$$

Eq. 4.6

In deriving this equation, $S_{20} = 0$ was used since $S_{20}$ is much smaller than $S_{10}$ for the uniaxially stretched electrostrictive PVDF films. Combining Eqs. 4.4 and 4.6 yields:

$$-s_{11}^m T_{2}^p A - s_{12}^m T_{1}^p A = s_{22}^m T_{2}^m + s_{12}^m T_{1}^m$$

Eq. 4.7

Since
It can be shown

\[ T^p_i = - \frac{A_{s_{11}}^m + s_{22}^m T^p}{s_{12} + A_{s_{12}}^m} \]  \hspace{1cm} \text{Eq. 4.8}

By combining these equations, one can arrive at the strain \( S_1 \) of the polymer film under the constraints of the electrode layers:

\[ S_1 \]

\[ S_{10} \]

\[ \frac{S_1}{S_{10}} = \frac{1}{1 + \frac{s_{11}(A_{s_{11}}^m + s_{22}^m) - s_{12}^m(s_{12}^m + A_{s_{12}}^m)}{A_{s_{11}}^m(A_{s_{11}}^m + s_{22}^m) - s_{12}^m A(s_{12}^m + A_{s_{12}}^m)}} \]  \hspace{1cm} \text{Eq. 4.10}

To further simplify Eq. 4.10, we assume the Poisson’s ratios for the terpolymer and the electrode layer to be approximately 0.4 and 1/3, respectively. One can also introduce

\[ B = \frac{Y_p}{Y_m} = \frac{s_{11}^m}{s_{11}} \]  \hspace{1cm} \text{Eq. 4.11}

where \( Y_p \) and \( Y_m \) are the Young’s moduli of the polymer film along the stretching direction and electrode layer and \( s_{11} = \frac{1}{Y_p} \) and \( s_{11}^m = \frac{1}{Y_m} \). For the terpolymer, the elastic compliance \( s_{22} \) perpendicular to the stretching direction is about 5 times of elastic compliance \( s_{11} \) along the stretching direction. Substituting these into Eq. 4.10, one can arrive at

\[ \frac{S_1}{S_{10}} = \frac{1}{1 + \frac{(AB + 0.2) - 0.4(0.4 + 0.33AB)}{AB(AB + 0.2) - 0.33AB(0.4 + 0.33AB)}} \]  \hspace{1cm} \text{Eq. 4.12}
Eq. 4.12 indicates that the degree of reduction in $S_1$ is related to both the thickness ratio and the ratio of Young’s moduli between the polymer and the electrode. Figure 4-13 illustrates how the ratio of $S_1/S_{10}$ changes with total electrode thickness for the metal electrode (Au, for example, has $Y=79$ GPa) and conductive polymer electrode ($Y=1$ GPa) for the terpolymer films with thickness of 5 $\mu$m and 10 $\mu$m, respectively. The elastic modulus of the terpolymer film along the stretching direction is 0.5 GPa. The results show the advantage of using conductive polymer electrodes in reducing the electrode mechanical constraint effect to the EAP film strain responses. For the conductive polymer layer thickness in 0.1 to 0.2 $\mu$m range, the reduction of the strain of terpolymer films of 5 to 10 $\mu$m thick is quite small. However, when the conductive polymer layer thickness is comparable to that of terpolymer films, the strain reduction can be quite significant. These results are consistent with the experimental data.
Figure 4-13: The dependence of the strain ratio of $S_1/S_{10}$ on the electrode thickness for Au electrode (+) and conductive polymer electrode (o) for EAP film thickness (a) $t_p=10 \, \mu\text{m}$ and (b) $t_p=5 \, \mu\text{m}$. 
4.5 Self-Healing Effect in PVDF-TrFE-CFE Terpolymer Films

For EAP devices operated under high electric field, electric breakdown in EAP films is a concern. Such an electric breakdown may cause shorting between two electrodes and consequently catastrophic failure of the EAP actuators. For EAP Braille actuators, it is highly desirable to have self-healing or graceful failure after electric breakdown. That is, in the event of electric breakdown, the adjoining thin conductive electrodes evaporate and the defect thus becomes isolated, as schematically illustrated in Figure 4-14. As a result, the EAP actuator will only lose very small portion of the film after breakdown while still maintaining the actuation capability. In fact, in the polymer film capacitor industry, self-healing is used to remove weak spots in the films prior to the assembly of the films into capacitors.

There are several mechanisms that can result in self-healing or graceful failure in polymer films. One mechanism is due to local heating at the breakdown spot, which can cause evaporation of the electrodes in the surrounding region and leave an area around the breakdown spot without conductive electrodes. Figure 4-15 shows the Thermal Gravimetric Analysis measurement of PEDOT conducting polymer film by using a TA Instrument SDT Q600. It shows that the decomposition temperature of PEDOT film is 350 °C, which is much smaller than the melting temperature of Al (660°C). It is apparent that thin conductive electrodes with low melting temperature will make it easier for the self-healing to occur. In most of the earlier works on self-healing, the electrode used is aluminum, zinc, or zinc-aluminum alloy, because of their relatively low melting temperatures. The much lower decomposition temperature of the conductive polymer and
the thin electrode layer developed here will lead to better self-healing behavior than these metal electrodes.

Figure 4-14: Schematic of the electric breakdown process which produces self-healing.

Figure 4-15: The percent weight loss of PEDOT film as a function of the temperature by TGA.
4.5.1 The change of capacitance and dielectric loss during the self-healing process

In addition to the vaporization of the electrode layer in the self-healing process, it is also crucial that the polymer in the breakdown process decomposes to gaseous byproducts rather than graphite. The formation of graphite will lead to increased conduction at the breakdown region of the polymer, which will result in the failure of EAP devices. In our experiment, it was observed that the presence of weak spots causes higher dielectric loss. Breakdown at these spots removes these weak spots and the self-healing after breakdown leads to terpolymer films with reduced dielectric loss and higher operation fields than before the self-healing.

Figure 4-16 summarizes the changes in capacitance and dielectric loss for the terpolymer films with conductive polymer electrodes before and after breakdown. The data show a large reduction of the dielectric loss after the self-healing, indicating: (i) the weak spots in the films which contribute to the conduction loss have been removed through the self-healing breakdown process and (ii) the breakdown by-products are not conductive, i.e., there is no graphite formation. The data also show that there are reductions in the capacitance, which are due to the reduced area of the film samples after self-healing breakdown. The optical micrographs of the burn-out areas after self-healing breakdown are shown in Figure 4-17. For some small film samples, these areas can be more than 10% of the total area as shown in Figure 4-14. With improved film quality, the weak spots can be reduced markedly as in the commercial polymer film capacitors. The result here is consistent with earlier studies.23
Figure 4-16: The change in dielectric loss and capacitance of the (PVDF-TrFE-CFE) films following self-healing. Shaded bars: the dielectric properties before the self-healing breakdown; black bars: the dielectric properties after self-healing.

Figure 4-17: An optical microscope image of a self-healing breakdown in the terpolymer film coated with conducting polymer electrode.
4.5.2 Weibull distribution function and dissipated energy during the self-healing

Before discussing the dissipated energy, we will introduce briefly the Weibull distribution function utilized to analyze the dissipated energy and breakdown field during the self-healing. The Weibull distribution is an engineering method of statistical analysis for recurring events, such as those that involve the lifetime of a component in a system. It is widely used in problems involving the failure rate, the reliability of a product and the lifetime distribution.\textsuperscript{24}

The Weibull distribution is usually written as

\[ F(x) = 1 - e^{-\left(\frac{x}{\alpha}\right)^\beta} \] \hspace{1cm} \text{Eq. 4.13}

which can be transformed to:

\[ \ln(\ln\left(\frac{1}{1 - F(x)}\right)) = \beta \ln x - \beta \ln \alpha \] \hspace{1cm} \text{Eq. 4.14}

where if one set ln x as the independent variable X, this function becomes a straight line, where \( \beta \) corresponds to the slope of the line and \( \beta \ln \alpha \) is the intercept of this line. In Weibull analysis, \( \alpha \) and \( \beta \) are called the characteristic life and shape parameters, respectively.

The Weibull characteristic life parameter \( \alpha \) is a measurement of the spread in the distribution data. For example, in the following self-healing voltage test, \( \alpha \) is the voltage where 63.2 percent of the samples have experienced self-healing.

At first, to measure the self-healing voltage, the electrode of the film sample is printed by screen printing method. This setup is shown in Figure 4-18.

In the screen printing of the conductive polymer electrodes, the polymer film is
placed underneath the screen. Then, a drop of PEDOT conducting polymer solution is
dipped on the screen surface and brushed by the rubber brush shown in this picture.
Afterwards the printed polymer film needs to dry in an oven for a few minutes. By
varying the concentration of the conducting polymer solution, the electrode thickness can be varied from the nanometer range to several µm.

The self-healing electrical fields of these samples were tested and the data is shown in Table 4-1. Figure 4-19 shows a Weibull analysis of the self-healing voltage of these samples, where the shape parameter β is 2.93, which indicates the samples that are the typical wear-out samples. The characteristic field α is 80.2 MV/m, which means most of samples have self-healing occurring at this field.

Figure 4-18: The screen printing setup for conducting polymer electrode
Table 4-1: The self-healing electrical field (MV/m) for screen printed conducting polymer electrode (200 nm).

<table>
<thead>
<tr>
<th>Self-healing Electrical Field</th>
<th>Sample</th>
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<tbody>
<tr>
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<td>116.5</td>
<td>14</td>
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</table>

Figure 4-19: Weibull analysis of the self-healing electrical field (MV/m) of terpolymer sample using screen printed conducting polymer electrode (200 nm).
Compared with early results, this electrical field for breakdown seems low. It may come from the damage to these very thin polymer films (8 µm) during the screen printing process. To improve the breakdown voltage (self-healing voltage), a non-contact printing method is developed. A spray probe controlled by an ultrasonic atomizer (Sonaer Inc, Farmingdale, NY) is used to deposit the thin electrode on the polymer surface. After the deposition, the electrode is about 200 nm. Then, the self-healing voltage is measured and the self-healing data is shown in Table 4-2.

The self-healing voltages in these 10 samples are analyzed using Weibull analysis and results are shown in Figure 4-20. The Shape Parameter (β) and Characteristic field are improved to 3.2 and 131MV/m, respectively.

For the screen printed electrode, self-healing voltage is about 80.2MV/m. From the result in Figure 4-20, the self-healing voltage of the sprayed electrode is 131 MV/m, which is much improved. This indicates that the spraying process removes the damages caused by the direct contacting screen printing process and improves the breakdown field.
Table 4-2: The self-healing electrical field (MV/m) for the sprayed conducting polymer electrode (200 nm).

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<tr>
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<td>8</td>
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<tr>
<td>130.8</td>
<td>9</td>
</tr>
<tr>
<td>228.6</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 4-20: Weibull analysis of the self-healing field (MV/m) using the sprayed conducting polymer electrode (200 nm).
Another important parameter that needs to be considered is the dissipated energy of the self-healing. A small energy for self-healing is highly desirable since it will cause less damage to the polymer film after breakdown. From the early results, Shaw, Cichanowski, and Yializis had shown the relation of the self-healing energy related to the electrode thickness at zero interlayer pressure to be\(^{25}\)

\[
U \propto t^{1.8}
\]  
Eq. 4.15

This relation seems to be valid for the aluminum electrode. Here, we will examine whether this is also applicable to the conducting polymer electrode, and consider the relation of the dissipated energy to the conducting polymer electrode thickness.

First, for a 100 nm electrode, the dissipated energies of self-healing are measured by Sawyer–Tower circuit. Shown in Figure 4-21(a) is the current spike associated with a breakdown event in a terpolymer film and it is apparent that after breakdown, the film capacitor remains insulating under the high voltage. In order to prevent the air breakdown in these breakdown tests, the EAP films were dipped into the silicon oil to provide a thin insulation oil layer on the films prior to the breakdown tests. The total charge associated with each breakdown event was also measured using a modified Sawyer-Tower circuit and a typical data is shown in Figure 4-21(b), where the breakdown event causes a sudden increase in the charge density. The energy \( U \) consumed during the breakdown can be found from:

\[
U = \rho_q A V
\]  
Eq. 4.16
where $\rho_q$ is the change of the charge density, $A$ is total sample area, and $V$ is the applied voltage. The dissipated energy during the self healing event in Figure 4-21(b) is about 0.15 mJ. The thickness of the polymer film and the electrode are about 27 $\mu$m and 0.1 $\mu$m, respectively. The total electrode area is about 1.5 cm$^2$ for all the samples. Tests were conducted for many other polymer samples with the same conductive polymer electrode thickness and area. The dissipated energy data for the 100 nm electrode samples is shown in

The Weibull Analysis data of these data is shown in Figure 4-22, where the shape parameter $\beta$ is 0.81 and the characteristic life parameter $\alpha$ is $87 \times 10^{-6}$ J, respectively. This means that the average dissipated energy for a 100 nm conducting polymer electrode is about 87 $\mu$J.
Figure 4-21: a) The current spike during the self-healing breakdown and b) The charge density jump associated with a breakdown (DC Voltage is 3900 V and the thickness of terpolymer film is 27 µm).
Figure 4-22: Weibull analysis of the self-healing energy (µJ) using the sprayed conducting polymer electrode (100 nm). Solid point, the experiment data and solid line, the linear fitting of the experiment data.

Table 4-3: The dissipated energy for the sprayed conducting polymer electrode of thickness of 100 nm.

<table>
<thead>
<tr>
<th>Energy (µJ)</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.55</td>
<td>1</td>
</tr>
<tr>
<td>27.4</td>
<td>2</td>
</tr>
<tr>
<td>27.5</td>
<td>3</td>
</tr>
<tr>
<td>42.3</td>
<td>4</td>
</tr>
<tr>
<td>153</td>
<td>5</td>
</tr>
<tr>
<td>259</td>
<td>6</td>
</tr>
</tbody>
</table>
For 200 nm electrode, the dissipated energy is also measured by Sawyer–Tower circuit and the data is shown in Table 4-4. The Weibull Analysis data for the 200 nm thickness electrode is shown in Figure 4-23, where the shape parameter $\beta$ and the characteristic life $\alpha$ are 0.72 and $997\times10^{-6}$ J, respectively. Therefore the average dissipated energy for the 200 nm conducting polymer electrode is about 0.997mJ.

Relative to the 100 nm electrode, the dissipated energy for the 200 nm electrode is much larger. This arises from the difficulty of the thick electrode to evaporate during the self-healing process. It is reasonable that the thick electrode requires more energy to clear during the self-healing process. Our data seems to be consistent with Eq. 4.15.

The dissipated energy for a 200 nm electrode is in the range of 0.1 mJ, which is much lower than the aluminum electrodes. This is understandable since the aluminum electrodes have much higher melting temperature (~660 °C). This means that the self-healing occurs more easily when the conducting polymer is used as the electrode of the polymer. Based on those results and the clamping effects associated with the meal electrodes, we selected the conducting polymer as the electrode for our actuator.

The relationship of clearing energy to applied voltage at zero pressure can be derived in the following:

$$U = \rho_{q}AV = \frac{CV}{A}AV = CE^{2}\frac{t_{p}}{E^{2}t_{p}} = \frac{\varepsilon A}{t_{p}}E^{2}t_{p}^{2}$$

where $U$ is dissipated energy during self-healing process, $V$ is applied voltage, $C$ is polymer sample capacitor, $\varepsilon$ is dielectric constant of the polymer sample, $A$ is polymer sample area, $t_{p}$ is the polymer thickness, and $E$ is the self-healing electrical field. From
this equation, it is revealed that the dissipated energy is also proportional with the polymer thickness and the dielectric constant of the polymer material.

Table 4-4: The dissipated energy for the sprayed 200 nm conducting polymer electrode.

<table>
<thead>
<tr>
<th>Energy (mJ)</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>1</td>
</tr>
<tr>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td>0.19</td>
<td>3</td>
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<td>0.29</td>
<td>4</td>
</tr>
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<td>0.43</td>
<td>5</td>
</tr>
<tr>
<td>0.97</td>
<td>6</td>
</tr>
<tr>
<td>1.2</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 4-23: Weibull analysis of the self-healing energy (mJ) using sprayed conducting polymer electrode (200 nm). Solid point, the experiment data and solid line, the linear fitting of the experiment data.
4.6. The EAP Braille Actuator

Terpolymer films with thin conductive polymer electrodes and after self-healing breakdown were wound around a pre-stressed thin spring to form a Braille actuator. A schematic of the fabrication process is presented in Figure 4-24. As shown in Figure 4-12, the terpolymer film elongates under an electric field, which when combined with a pre-stressed spring core (compressive stress) will push the Braille dot up. Upon removing the electric field, the Braille dot returns to original position.

A winding machine was designed and built for the fabrication of the EAP Braille actuator, which provides pre-stress in the spring core and better control of the fabrication process. In the current design, the EAP film thickness is ~5-6 µm. To separate the two electrodes on the two faces of the EAP films in the wound actuator, the electroded polymer films were bound together by employing the residual solvent in the films (the solvent content is in 1 % to 2 % range) under high pressure and at an elevated temperature to form a bilayer (see Figure 4-24(d)). In the thermal fusing process, the two thin EAP films were heated to 80 °C under a 1000 lb force (3.6 MPa) for 20 minutes to bond the two layers together. To ensure correct electrical connection as well as good bonding, the capacitance and the total bilayer film thickness were measured. The total capacitance should be the sum of the capacitance of each layer. The bilayer film was wound on the spring core to form the Braille actuator. A commercial spring, spring probe ICT-100 (Interconnect Devices Inc, Kansas City, KS), was chosen as the core on which the EAP film is wound. The diameter of the spring core is 1.37 mm and the total length is 60 mm. The spring constant is about 225 N/m. After winding, both ends of the EAP film
are glued to the spring by Devcon 5-minute epoxy (Riviera Beach, FL). Care has to be taken in handling very thin polymer films in this fabrication process to ensure that the films are not damaged. The total length of active polymer film is about 34 mm and Figure 4-25 presents a photograph of a finished actuator.

The Braille actuator performance was characterized by displacement, as measured by a CCD camera. The strain data are shown in Figure 4-26. The data shows that the total displacement of actuator is 1mm under 100 MV/m, which corresponds to 3 % strain in the EAP film and is consistent with the strain data in Figure 4-12. The result indicates that the EAP film performs well in the Braille actuator configuration. For a Braille display, the minimum dot displacement is 0.5 mm and hence, the compact Braille actuator developed here is more than adequate to meet the displacement requirement of the Braille dots. The force level of the finished actuator is also evaluated by weight scale Adventurer SL, AS214 (Ohaus Corporation, Pine Brook, NJ). The data are shown in Figure 4-27. It was found to push back the actuator in 0.5 mm displacement requires a force of 1.1 N. For a typical refreshable Braille displays, the force level of the dots is in the 0.1 to 0.5 N range. Therefore, the EAP Braille actuator meets all the functional requirements of refreshable Braille display, as well as offering compact size, reduced cost, and light weight.
Figure 4-24: Schematic of fabrication process of the rolled EAP actuator for Braille display using the electrostrictive polymer thin films: (a) Pre-strained spring core, (b) electroded polymer thin film, (c) thin film folded to form a bilayer to separate the positive and negative electrodes, and (d) the rolled actuator.

Figure 4-25: Picture of the EAP Braille actuator
Figure 4-26: Displacement of the tip (the Braille dot) of the Braille actuator.

Figure 4-27: Blocking force of the Braille Actuator. Solid point, experiment data and solid line, a linear fitting to the experiment data.
4.7 Summary

In conclusion, it was demonstrated that an actuator based on the electroactive terpolymer P(VDF-TrFE-CFE) can provide much better performance than the Braille actuator based on piezoceramics. During the development of the EAP Braille actuators, a sprayed conductive polymer electrode was found, which can form thin (less than 0.1 µm thick) conductive polymer electrode with strong bonding to the EAP films and is suitable for mass production of the Braille actuators. It was further shown that the small thickness, the low melting temperature of the conductive polymer, as well as the unique chemistry of the conductive polymer used all result in a self-healing capability of the EAP films after an electric breakdown. The self-healing electric breakdown process removes weak spots in the EAP films and the resulting films can sustain high voltage and function properly. The final EAP Braille actuator generates a dot displacement of 1 mm with a force level more than 0.75 N. By reducing the EAP film thickness from the current 6 µm to below 3 µm, the Braille actuator can be operated under 200 volts, which is the voltage employed in the current piezoceramic single line refreshable Braille display.
References:


CHAPTER 5
THE THERMALLY CONTROLLED HYBRID EAP/SMP ACTUATOR

5.1 Introduction

Shape Memory Polymers (SMP) are a class of active polymers which have a broad range of applications, including medical devices, deployable aerospace structures, Microsystems and autochoke for engines.\textsuperscript{1-7} Several key features of SMPs make them attractive for these applications. One key feature is the large elastic modulus change as a SMP passes through the glass transition $T_g$, where the SMP exhibits more than several orders of magnitude change in the elastic modulus over a relatively narrow temperature interval around its $T_g$.\textsuperscript{2}

Another key feature is the shape memory effect. That is, the SMP can be shaped into an arbitrary configuration at a temperature $T$ higher than $T_g$, by holding the SMP into this configuration and reducing the temperature to below $T_g$, the SMP can keep the given configuration without any external forces at temperatures below $T_g$. This feature is schematically illustrated in Figure 5-1. At $T > T_g$ ($T_g = T_{\text{trans}}$), the SMP is strained to $S_m$ under a stress $\sigma_m$. Then, the temperature is decreased to below $T_g$ while the SMP is under this stress and strain. At $T < T_g$, when the external stress is removed, the SMP can retain this strain $S_m$. This second feature allows one to store a high elastic energy density and realize very high actuation capability in the SMP.
There are many applications that can utilize the reshaping ability of an SMP. In this chapter of my thesis, our purpose is to integrate SMP with another active material to form a hybrid actuator that can change shape through temperature cycles, as schematically illustrated in Figure 5-1, and can also retain a high strain level with a high elastic modulus at temperatures below its $T_g$. By employing another active material which can reshape and impart strain to the SMP at $T > T_g$, the SMP can have variable memory states at $T < T_g$.

Figure 5-1: The schematic representation of the results of the cyclic thermomechanical investigations of SMP. (1): at $T > T_{trans}$ ($T_{trans} = T_g$), SMP is strained to $S_m$; (2): cooling below $T_{trans}$ while strain $S_m$ is kept constant; (3): removing stress, SMP can still retain the strain $S_m$ (memory effect)
5.2 Characterization of the Hybrid SMP/EAP Actuator

5.2.1 The working principle of the hybrid SMP/EAP actuator

The integration of shape memory polymers (SMP) and electroactive polymers (EAP) creates a new class of multifunctional actuators with large strain and shape change capabilities, high stress levels, and a shape memory effect. Here we investigate a hybrid actuator that makes use of the large strain change in a ferroelectric polymer to tune the strain and shape of SMP at temperatures above the glass transition of SMP. By cooling to below $T_g$ of the SMP, the actuator retains the strain and shape change with a high force level due to the large elastic modulus of SMP below $T_g$. Since the strain $S$ in an SMP is imparted at $T > T_g$ by another active material, which here is a ferroelectric P(VDF-TrFE) copolymer, there are many orders of magnitude increase in the elastic modulus $Y$ of SMP, and hybrid actuators can generate a very high elastic energy density $U_0$. By varying the temperature cycle, the strain and shape of the hybrid actuator can be varied over a large range, while concomitantly being precisely controlled by another active material. Furthermore, it is possible to utilize a composite approach of strain anisotropy as well as large elastic modulus anisotropy in the hybrid actuator, i.e., the elastic modulus along one direction is orders of magnitude higher than in the other directions. Such variable properties can be potentially exploited for a broad range of applications, such as in biomedical devices and morphing aircraft wing.

As discussed in Chapter 1, a large lattice strain can be generated by varying the temperature across the F-P transition of PVDF-TrFE copolymer (below the transition, it is ferroelectric and above the transition, it is paraelectric). Furthermore, the first order
nature of the transition also results in a large thermal hysteresis (more than 30 °C for this composition, and it will increase with VDF/TrFE ratio), which is an attractive feature of the hybrid actuator.11

In addition to electric fields, the high temperature point of the temperature cycle can also be used to control the strain level in the P(VDF-TrFE) copolymer, and consequently the strain and shape of SMP. This is illustrated in Figure 5-2. Assuming a total strain change of 3.3 % through the whole F-P transition hysteresis, by stopping the transition at a temperature below the $T_{\text{max}}$, a smaller strain hysteresis will be produced. In the figure, strain hysteresis cycles for 2 % strain and for 1 % strain are illustrated.

One configuration of this hybrid actuator is a unimorph structure as illustrated schematically in Figure 5-3. The large strain along the polymer chain direction in the EAPs enables a large bending motion in the unimorph (along the chain direction, the polymer shrinks as it goes from low temperature to high temperature through the F-P transition). As the temperature of the actuator is raised from below to above the F-P transition of EAP and the $T_g$ of SMP, the EAP generates a negative strain. Because SMP’s elastic modulus is much smaller than that of EAP at high temperatures, the SMP will also be strained to this level. When cooling down to $T < T_g$ and $T > T_{F-P(\text{cooling})}$ (see Figure 5-4), the SMP will remember this strain change. When further cooling down to $T < T_g$ and $T < T_{F-P(\text{cooling})}$, the SMP retains the strain and the EAP expands back to the initial strain state. The unimorph will change its shape from the initial flat configuration to the final curved configuration. The curvature of the unimorph can be controlled by manipulating the strain in EAP above $T_g$. 
Figure 5-2: The temperature dependence of the thermal expansion strain of PVDF-TrFE. $T_{\text{max}}$ is the temperature of maximum strain.

Figure 5-3: An illustration of the bending actuation of a hybrid actuator of an SMP and an EAP.
First of all, we would like to determine the composition of the PVDF-TrFe polymer so that the transition temperature of the EAP matches the glass transition temperature of the SMP and the working principle of the SMP/EAP hybrid actuator as illustrated in Figure 5-4. The different compositions of PVDF-TrFe copolymers were characterized by differential scanning calorimetry (DSC) to determine the $T_{F-P}$ (heating) and $T_{P-F}$ (cooling). DSC was carried out with a TA Q100 instrument (TA Instruments Inc.) at a heating rate of 10 °C/min. DSC scans for PVDF-TrFe copolymer are shown in Figure 5-5, including the compositions from 50/50 to 81.7/18.3.

From the DSC data, during the heating process, as the ratio of PVDF/TrFe is increased, $T_{F-P}$ (heating) slowly shifts to high temperature with the ratio of PVDF...
79.6/20.4, at which $T_{F-P}$ (heating) is preempted by the melting transition. This is consistent with the phase diagram of PVDF-TrFE in Chapter 1.\textsuperscript{10} In the hybrid actuator, the existence of $T_{F-P}$ (heating) is necessary to generate the large strain through the transition. Thus, the concentration of PVDF must to be less than 79.6/20.4 in the PVDF-TrFE to match the requirement for the hybrid actuator. The next requirement for the hybrid actuator is the temperature condition. To have a large bending of actuation during the thermal stimulated process, there should be a large hysteresis between the F-P transition temperature $T_{F-P}$ of the heating process and P-F transition temperature $T_{P-F}$ of the cooling process. The glass transition temperature of the SMP will be between the $T_{F-P}$ (heating) and $T_{P-F}$(cooling) to enable a large actuation.

---

**Figure 5-5:** The DSC data heating scans of the PVDF-TrFE copolymer for the various PVDF compositions. (The lower T and higher T endotherms indicate phase transition temperature $T_{F-P}$ and melting temperature $T_m$, respectively.).
Furthermore, the DSC data during cooling in Figure 5-6 is examined for a suitable P-F temperature $T_{P-F}$. From the data, the temperature $T_{P-F}$ for all the compositions of PVDF-TrFE is in a range of 59 to 66 °C. The composition dependence of the temperature hysteresis $\Delta T$, defined as $T_{F-P(heating)}$ - $T_{P-F(cooling)}$, is shown in Figure 5-7. From the data, it is obvious that the temperature hysteresis $\Delta T$ slowly increases with VDF/TrFE ratio. To have the largest temperature hysteresis $\Delta T$ to satisfy the condition in Figure 5-4, PVDF-TrFE 75/25 is chosen to be the active material of hybrid actuator. It is possible to have another composition which is better than PVDF-TrFE 75/25. The composition of PVDF should be between 75/25 and 79.6/20.4 based on the experimental data. However, this composition is not commercially available.

Figure 5-6: The DSC cooling scan for the PVDF-TrFE copolymer in various compositions, where the lower and higher T exotherms indicate phase transition temperature $T_{P,F}$ (cooling) and crystallization temperature $T_c$, respectively.
PVDF-TrFE 75/25 was further characterized by dynamic mechanical analysis (DMA). DMA was performed with a TA DMA 2980 instrument in the step-scan and tensile mode with frequencies from 20 to 0.1 Hz. Samples for DMA are relatively thick (~100 µm). The data is shown in Figure 5-8. From the data, there is an obvious maximum in the loss tangent around 95 °C. Meanwhile, the Young’s modulus decreases from 2.06 GPa at 30 °C to 26 MPa at 95 °C, a decrease of about 2 orders of magnitude. This means that the glass transition temperature of SMP is around 95 °C, and it is located between the \( T_{F,P} \) (116.4°C) and \( T_{P,F} \) (66.2°C) of PVDF-TrFE 75/25.

As a comparison, the Young’s modulus data for both SMP and EAP are shown in Figure 5-9. From the data, it is clear that the Young’s moduli of both SMP and EAP have approximately the same value in the room temperature. When the temperature increases
to more than 80 °C, the Young’s modulus of the SMP decreases sharply while that of the EAP decreases a small amount. This indicates that the EAP is much stiffer at high temperatures than the SMP.

As mentioned previously, during the heating process when the temperature is higher than T_g of SMP the SMP becomes very soft and can be reformed in the shape of the EAP. As the temperature increases above the F-P transition temperature T_{F-P} of the EAP, the EAP contracts about 3.3 %. Due to the very low Young’s modulus of SMP, the whole device would contract at that temperature. Consequently, when the temperature is cooled down from 120°C and to below the T_g of the SMP at 95°C, the SMP would recover to high elastic modulus and retain the -3.3% strain generated by EAP in the heating process. When the temperature continues to decrease below the P-F temperature T_{P-F} of EAP, the EAP would expand back to the original length. Meanwhile, the SMP have already shrunk and is in memory state. From the working principle of the unimorph

Figure 5-8: The temperature dependence of the Young’s Moduli and the mechanical loss tangent of SMP at 1 Hz.
structure, the whole actuator device would generate large bending associated with this
3.3\% expansion strain from PVDF.

\[
\kappa = \frac{1}{R} = \frac{6AB(1+B)d_{31}E_3}{t_{EAP}(A^2B^4 + 2A(2B + 3B^2 + 2B^3) + 1)} \quad \text{Eq. 5.1}
\]

where A is the ratio of the Young’s modulus \(Y_{SMP}/Y_{EAP}\), B is the thickness ratio of \(t_{SMP}/t_{EAP}\), \(d_{31}\) is the piezoelectric coefficient of piezoelectric material, and \(E_3\) is the electrical field.

Figure 5-9: Comparison of the Young’s Moduli of the SMP and EAP at 1 Hz.

5.3 An Analysis of the Hybrid SMP/EAP Actuator Performance

The equation related to the unimorph actuator had been derived by Q. M. Wang and the curvature of this structure is related to the strain level generated from the EAP and other materials parameters and dimensions as: \(^{15}\)
For the actuator here, Eq. 5.1 can be rewritten as:

$$\kappa = \frac{1}{R} = \frac{6AB(1+B)S}{t_{EAP}(A^2B^3 + 2A(2B + 3B^2 + 2B^3)+1)}$$

Eq. 5.2

where $S$ is strain. This equation is in a more general form.

The curvature as a function of the thickness ratio $B$ is shown in Figure 5-10. The parameters used in the calculation are shown in Table 5-1.

The figure reveals that the maximum curvature of the actuator can be obtained by adjusting the thickness ratio of $t_{SMP}/t_{EAP}$. We can consider two extreme cases in this situation. At first, when the thickness of the EAP changes to zero, which means that no momentum is applied to the actuator, the total curvature of the actuator is zero. Then, when the thickness of SMP changes to zero, the holding force from the SMP is zero when the EAP expands. This means that the EAP expands by itself and there no bending occurs. The ideal condition should exist between these two extremes to obtain the largest curvature of actuator.

Table 5-1: Parameters used in curvature calculation of the SMP/EAP actuator.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s Modulus (GPa)</th>
<th>Thickness (µ m)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape Memory Polymer</td>
<td>2.06</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>Electroactive Polymer PVDF-TrFE</td>
<td>1.66</td>
<td>100~500</td>
<td>3% or 2%</td>
</tr>
</tbody>
</table>
5.4 The Experiment

5.4.1 Fabrication and Performance of Actuator

Data in Figure 5-10 indicate that the largest curvature occurs when the thickness ratio of the SMP with EAP is around 1.8. When the thickness of SMP is around 350 µm, a 175 µm thickness of the EAP film generates the largest bending of the actuator.

Due to high crystallinity of the PVDF-TrFE polymer, it is difficult to stretch the film when the thickness of PVDF-TrFE is more than 100 µm. Thus, all the films are fabricated below 100 µm and then glued together. PVDF-TrFE films were first fabricated by the solution cast method. To get orientation of the stretched film, zone-drawing was used. Zone drawing equipment shown in Figure 5-11 was developed by
Strategic Polymer Science Inc. (State College, PA). In this method, there are two computer controlled motors. The speed of front motor can be set to 5 times the speed of the back motor to stretch the film to 5 times. A heating element is placed between the front and back motors. During the drawing, the back motor is also moving at a slow speed to allow all the stretching parts to heat uniformly. Finally, by controlling the drawing speed and heating temperature, we can get large uniform piece of PVDF-TrFE film.

The next step is to fabricate the EAP/SMP actuator. The fabrication process is shown in Figure 5-12. After the drawing, the thickness of EAP is about 20 μm. Pairs of the films are glued by epoxy Insulgel 50 (Insulcast Co. Ltd) to become a multilayer film around 180 μm. Afterwards, the whole sample is allowed to dry at room temperature for 72 hours to cure the epoxy.

Figure 5-11: The zone-stretching apparatus.
The SMP film (thickness 350µm) is supplied by Cornerstone Research Group (Dayton, Ohio). It is cut into 26 mm × 10 mm sheets. The surface of the SMP is then polished by a rough polish paper to allow for good interfacial contact.

In the final step, the SMP is glued together with EAP multilayer by Heat Resistant Sealant 736 (Dow Corning Co. Ltd), which can be used under continuous exposure to 260 °C. For our application, the temperature of application will not exceed 150 °C, which is in the working range of this Sealant. The whole actuator is cured at the room temperature for 24 h and the fabrication of hybrid actuator is complete.

During the experiment process, the hybrid SMP/EAP actuator is heated in silicon bath oil, which is stirred by a circulation fan to keep a uniform temperature of the whole chamber. The bath is heated at step of 5 °C/min to 120 °C. After that, the heating chamber is cooled down by the chilled water at step of 3 °C/min to room temperature.

Figure 5-12: The fabrication process of hybrid SMP/EAP actuator: (a) stretched PVDF-TrFE (EAP) films, (b) multilayer film of PVDF-TrFE glued by Sulgel50, (c) a large sheet of shape memory polymer, (d) the small cut piece of SMP and (e) the EAP and SMP films bonded together by Heat Resistant Sealant 736 to form a hybrid actuator.
Finally, we find that the actuator is bent to a curved shape and retains that shape. The picture of the actuator before and after experiment is shown in Figure 5-13(b), where the thickness of SMP and EAP are 352 µm and 185µm, respectively, so the thickness ratio of the SMP with EAP is 1.89. The length L of actuator is 32.2 mm.

The method of the curvature calculation is shown in Figure 5-14. From the diagram, the equation related to the radius of arc is:

\[
\left(\frac{l_0}{2}\right)^2 + (R-x)^2 = R^2 \tag{Eq. 5.3}
\]

Then, the radius R is calculated by:

\[
R = \frac{x^2 + l_0^2}{2x} \tag{Eq. 5.4}
\]

Using the dimension of the sample \(l_0 = 25.26\) mm and \(x = 9.31\) mm, from Eq. 5.4, the radius R is 13.22 mm. Then, from the definition of the curvature:

\[
\kappa = \frac{1}{R} \tag{Eq. 5.5}
\]

The curvature of the sample in Figure 5-13(b) is 75.6 m\(^{-1}\).

For this sample, the thickness ratio \(t_{\text{SMP}}/t_{\text{EAP}}\) is 1.88, which is close to the optimal condition \((t_{\text{SMP}}/t_{\text{EAP}} \sim 1.8)\) of the actuator. From the theoretical calculation in Figure 5-10, the largest curvature of actuator at the 3% strain of EAP is about 72 m\(^{-1}\), which is very close to our measurement. Finally, it is clear that the theoretical calculations fit very well with the experiment, which means that the actuator is functions successfully.
Figure 5-13: The hybrid EAP/SMP actuator at (a) the initial condition $S=0$ and (b) after heating to 120°C and cooled to room temperature. The thickness ratio $t_{SMP}/t_{EAP}=1.89$.

Figure 5-14: Diagram of the curvature calculation method for the hybrid EAP/SMP actuator.
5.4.2 The Effect of Glue on the Actuator

During the experiment, it was also found that the glue has a very critical effect on the performance of the hybrid actuator. At first, the epoxy used to glue the SMP with EAP is Insulgel 50, which is same as the glue used to fabricate the multilayer EAP sample. From reference, the working range of the Insulgel 50 is below 105°C, which is much below our experiment temperature (120°C). Thus, at higher temperatures, the glue will debond and the large interfacial force in the SMP-EAP interface during the bending will cause separation. A picture of the partially separated actuator is shown in Figure 5-15(a). Due to the debonding of the interface between the SMP and EAP, the curvature of the hybrid actuator is reduced.

Therefore, there are two requirements of the epoxy for the hybrid actuator:

1) Soft glue, which will not diminish the strain of the actuator.

2) A high temperature capability.

It was found that the silicon rubber Heat Resistant Sealant 736 (Dow Corning Co. Ltd) satisfied all the requirements. In the experiment, retains the bonding between SMP and EAP at the high temperature.

The actuator using Heat Resistant Sealant 736 is shown in Figure 5-15(b). Compared to the sample in 5-15(a), this sample bonds together very well at high temperatures and maintains large curvature. Using Eq. 5.2, the calculated strains of the samples in 5-15(a) and 5-15(b) are 1.53 % and 2.75 %, respectively. Debonding of the interface between SMP and EAP will impair the bending force generated from the electroactive polymer (EAP) and the curvature of the hybrid sample will be reduced.
However, the strain shown in 5-15(b) should be the real strain generated from this type of actuator at 110 °C.

5.4.3 The Thickness Ratio Effect in the Actuator

From the theoretical calculation in Figure 5-10, the thickness ratio has a critical effect on the curvature of the actuator. During the experiment, the thickness effect is tested by using the different thickness ratio of $t_{\text{SMP}}/t_{\text{EAP}}$ in the hybrid actuator. To verify the theoretical expectation, three samples are compared with thickness ratios $t_{\text{SMP}}/t_{\text{EAP}}$ of 1.06, 1.88, and 3.13. The samples are heated to 120°C and cooled down following the procedure discussed in this chapter. The picture of the bended sample is shown in Figure 5-16. Meanwhile, using Eq. 5.4, the calculated curvatures of these three samples are 65.5, 75.6 and 62.6, respectively. From the results, it is obvious that the largest curvature happened on $t_{\text{SMP}}/t_{\text{EAP}}$ around 2.
Figure 5-17 gives the comparison between the experimental data and the theoretical calculation data. From this figure, the experimental data fits very well with theoretical calculation data. It demonstrates that both the curvature of the hybrid EAP/SMP actuator theory are correct.

Figure 5-16: Hybrid actuators in different thickness ratios: (a) \( \frac{t_b}{t_a} (\frac{t_{SMP}}{t_{EAP}}) = 1/0.944 = 1.06 \), (b) \( \frac{t_b}{t_a} = 1/0.53 = 1.88 \) and (c) \( \frac{t_b}{t_a} = 1/0.32 = 3.13 \).

Figure 5-17: Experimental and theoretical calculation results for curvature ratio as a function of thickness ratio.
5.4.4 The Temperature-Tuned Actuator

From the thermal contraction data of PVDF in Chapter 1, the temperature will affect the strain of the electroactive polymer PVDF-TrFE. Thus, temperature can be optimized to control the strain of the actuator. The basic working principle is shown in Figure 5-2. From the diagram in this figure, when the sample is heated to the temperature $T_1$, where $T_1 < T_2$, the strain $S_1$ generated at $T_1$ should be smaller than the strain $S_2$ generated at temperature $T_2$. It is understood that when the temperature is only slightly lower than the Curie temperature $T_{PF}$ of PVDF-TrFE, the conversion from the ferroelectric to the paraelectric phase (F-P) is not totally accomplished. Part of the phase is still in the ferroelectric phase, and this part of the crystal will not generate contraction strain in the actuator. Until the temperature is increased above $T_{F-P}$, total F-P conversion does not occur.

A demonstration is shown in Figure 5-18, where same sample is heated to the temperatures 105 °C, 110 °C and 120 °C. It is evident that the sample curvature increases with increasing temperature. When the sample is heated to 120°C, the largest curvature occurs.

In this figure, the length of the sample and the thicknesses of the SMP and EAP are 32.33 mm, 352 µm and 185 µm, respectively. Using these dimensions, the calculated strains for the samples in Figure 5-18(a), (b) and (c) are 2.2 %, 2.75 % and 3.1 %, respectively. This demonstrates that the concept of using the temperature to tune the strain of the actuator is reasonable.

With this concept, we can fabricate a thermal tunable actuator using this EAP/SMP
hybrid structure, which has applications in the biomedical area.

Figure 5-18: Samples heated to the various temperatures and then cooled to room temperature: (a) heated to 105°C, (b) heated to 110°C, and (c) heated to 120°C.

5.5 Summary

In this chapter, the characteristics of the shape memory polymer (SMP) and electroactive polymer PVDF-TrFE 75/25 (EAP) were investigated. Based on these polymers, a hybrid actuator was investigated which utilizes of the large strain change in a ferroelectric polymer to tune the strain and shape of SMP at temperatures above the glass transition of SMP. By heating to more than 120 °C, the electroactive polymer experiences a negative strain and also the soft SMP is strained to the same level. By cooling to below T_g of the SMP, the shape memory polymer retains the strain and the electroactive polymer PVDF-TrFE expand to the original length, resulting in bending of the hybrid SMP/EAP actuator. Furthermore, we have demonstrated that the glue and the thickness ratio used in fabrication of the hybrid actuator are crucial in the performance of the actuator. Finally, it was demonstrated that this actuator can be tuned by the temperature to which it is heated.
References:


CHAPTER 6
CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

In this thesis, we have investigated approaches to significantly enhance the performance of several smart materials for actuators and electromechanical devices, with the objective of making smart materials smarter.

1) The very high electromechanical coupling factors of PMN-PT single crystals make them attractive for energy harvesting. 1-3 composites were investigated to improve the mechanical integrity while maintaining a high coupling factor. It was shown that 1-3 composites enable the single crystals to operate in the longitudinal mode to achieve high efficiency for energy harvesting, while the soft polymer matrix-supported single-crystal rods maintain high mechanical integrity under various external loads. Under a mechanical stress of 88.9 MPa at 4 Hz, a harvested power density near 0.1 W/cc (or an energy density of 25 mJ/cc) was achieved.

2) For energy harvesting, we investigated the concept of active energy harvesting, in which the electric boundary conditions are tuned to achieve higher system efficiency relative to the material efficiency. We discussed how to control the electrical boundary condition to maximize the energy conversion efficiency and the harvested electrical energy density in the electrostrictive polymers. As an example, it was demonstrated that when a properly phased and externally applied electric AC field is superimposed on the
mechanical cycle, an output electrical energy density of 39 mJ/cm$^3$ and a mechanical-to-electrical conversion efficiency of about 10% can be obtained from the P(VDF-TrFE) based electrostrictive polymers.

3) The large actuation strain and high elastic energy density of recently developed P(VDF-TrFE) based electrostrictive polymers show great potential for a broad range of solid state actuators. In this thesis, key issues related to the reliability of electroactive polymers PVDF-TrFE-CFE in the compact actuators and for the mass fabrication of these polymer actuators are investigated. Making use of a recently developed conductive polymer, a spraying method was developed which enables direct deposition of very thin conductive polymer electrode layers (< 0.1µm) that strongly bond to the terpolymer surface and require a short fabrication time. It was observed that the thin conductive polymer electrodes lead to self-healing of the polymer after electric breakdown. An EAP compact Braille actuator was designed and fabricated with these terpolymer films wound on a spring core. The test results demonstrate that the EAP Braille actuator meets all the functional requirements of actuators for refreshable full Braille display, as well as offering compact size, reduced cost and reduced weight.

4) For many applications, an electromechanical actuator is maintained in a strain (activated) state for a period of time. To maintain that strain state, an electric signal should be applied to the actuator. On the other hand, shape memory materials possess the capability for mechanical memory. By combining these two classes of smart materials, a hybrid actuator was developed where the actuation state can be tuned by the EAP and the actuated state can be maintained by the SMP without an applied electric signal. For the hybrid SMP/EAP actuator, we investigated a hybrid actuator which
makes use of the large strain change in a ferroelectric polymer to tune the strain and shape of SMP at temperatures above the glass transition of SMP.

We then demonstrated a concept which utilizes the thermal energy to control the strain of the hybrid SMP/EAP actuator. By heating to above $T_{F-P}$(heating), the electroactive polymer shrinks and drives the soft SMP to the same strain level. By cooling to below $T_g$ of the SMP, the shape memory polymer retains the strain while the electroactive polymer PVDF-TrFE expands to the original length, resulting in bending of the whole hybrid SMP/EAP actuator. By varying the temperature cycle, the strain and shape can be varied over a large range, while at the same time being precisely controlled, which makes it an attractive actuator for morphing aircraft. Furthermore, utilizing a nanocomposite approach, strain anisotropy as well as large elastic modulus anisotropy, i.e., the elastic modulus along one direction can be many orders of magnitude higher than other directions, can be realized in the hybrid actuator. Such variable properties can be potentially exploited to develop efficient skins which provide large strain changes for applications to new generation of morphing aircraft.

**6.2 Future Work**

There is still a significant amount of future work on all these research directions:

1) For the energy harvesting, more electrical boundary conditions can be analyzed and realized to maximize the energy conversion efficiency and harvested energy density. In the future, the stand-alone system is a good concept for the energy harvesting system to utilize the piezoelectric material to create DC bias field, thereby changing the electrical
boundary condition of the electrostrictive polymer to gain the high efficiency in the energy harvesting process.

2) For the solid state actuator, more work need to be done in reducing the thickness of the polymer film and eventually reducing the operation voltage of the actuator. The actuator can be better designed to increase the reliability of the product for future applications. The film should be fabricated in a clean room environment to improve the quality of the polymer film to enhance the reliability of the solid state actuator.

3) For the hybrid SMP/EAP actuator, thermal energy is utilized to control the strain of the actuator in this thesis. In the future, ideal design would allow an electric field to tune the actuation of the actuator, thereby broadening potential applications of this actuator.
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“Hybrid Actuator integrating Shape Memory Polymer with Electroactive Polymers, and other Active Polymer”, Inventor: Q. M. Zhang, Kailiang, Ren, Robert S. Bortolin and Jay Kudva.