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PVDF-BASED COPOLYMERS, TERPOLYMERS AND THEIR MULTI-COMPONENT MATERIAL SYSTEMS FOR CAPACITOR APPLICATIONS

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MINIATURE OF POWER ELECTRONICS, SCALING-DOWN OF MICROELECTRONICS AND OTHER ELECTRICAL AND ELECTRONIC SYSTEMS, AND DEVELOPMENT OF MANY TECHNOLOGIES (SUCH AS HYBRID VEHICLES OR IMPLANTABLE HEART DEFIBRILLATORS) REQUIRE CAPACITORS WITH HIGH ENERGY DENSITY TO IMPROVE THE WEIGHT AND VOLUME EFFICIENCY OF THE WHOLE SYSTEM. VARIOUS CAPACITOR TECHNOLOGIES ARE INVESTIGATED TO MEET THE REQUIREMENTS OF DEVELOPING FUTURE TECHNOLOGIES. AMONG THESE TECHNOLOGIES, POLYMER FILM CAPACITOR TECHNOLOGY IS ONE OF THE MOST PROMISING. BEIDES HIGH ENERGY DENSITY, POLYMER-BASED CAPACITORS POSSESS THE MERITS OF HIGH POWER DENSITY, LOW LOSS, HIGH RELIABILITY (SELF-HEALING), EASY PROCESSING, AND FEASIBILITY (IN SIZE, SHAPE AND ENERGY LEVEL).

DUE TO THE FERROELECTRICITY OF POLYVINYLIDENE FLUORIDE (PVDF)-BASED POLYMERS, THEY EXHIBIT MUCH HIGHER POLARIZATION RESPONSE UNDER AN ELECTRIC FIELD, IN COMPARISON WITH OTHER LINEAR DIELECTRIC POLYMERS FOR CAPACITOR APPLICATIONS. THE MAXIMUM POLARIZATION LEVEL OF PVDF-BASED POLYMERS CAN BE AS HIGH AS 0.1 C/m² AND THE BREAKDOWN FIELD CAN BE HIGHER THAN 600 MV/m. AN ESTIMATED ENERGY DENSITY OF AROUND 30 J/cm³ CAN BE EXPECTED IN THIS CLASS OF MATERIALS. HOWEVER, THIS VALUE IS MUCH HIGHER THAN THE ENERGY DENSITY THAT CAN BE ACHIEVED IN THE PVDF HOMOPOLYMER AND THE POLY(VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE) (P(VDF-TrFE)) COPOLYMERS DUE TO THE POLARIZATION HYSTERESIS IN THESE POLYMERS. THEREFORE, IN THIS THESIS, PVDF-BASED POLYMER MATERIALS WERE INVESTIGATED AND DEVELOPED TO APPROACH THIS EXPECTED ENERGY DENSITY BY VARIOUS STRATEGIES. AN ENERGY DENSITY OF HIGHER THAN 24 J/cm³, WHICH IS CLOSE TO THE PREDICTED VALUE, WAS FOUND IN PVDF-BASED COPOLYMERS.

RECENTLY, THE POLY(VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE-CHLOROFLUOROETHYLENE) (P(VDF-TrFE-CFE)) TERPOLYMER WAS DEVELOPED IN PROF. QIMING ZHANG’S GROUP. PREVIOUS WORKS HAVE SHOWN THAT INCORPORATION OF CTE INTO P(VDF-TrFE) COPOLYMERS, IN WHICH BULKY CFE ACTS AS A DEFECT, COULD CONVERT THE COPOLYMER INTO RELAXOR FERROELECTRICS. P(VDF-TrFE-CFE) TERPOLYMER POSESS A HIGH DIELECTRIC CONSTANT (LARGER THAN 50 AT 1 KHZ) AT ROOM TEMPERATURE AND EXCELLENT ELECTROMECHANICAL PROPERTIES.
Here, the P(VDF-TrFE-CFE) terpolymers were studied as dielectric materials for capacitor applications. The electrical, thermal and microstructure characterizations were performed on the terpolymers. The terpolymers exhibit a high breakdown field (higher than 400 MV/m) and energy density (larger than 9 J/cm³). The energy discharge characteristics of the terpolymer were studied by directly discharging the stored energy in the terpolymers to a load resistor. Due to the highly field-dependent nonlinear and frequency dependent dielectric response of the terpolymers, the discharge energy density and equivalent series resistance strongly depend on the load resistor and discharge speed. This study found that for high energy density dielectric materials, a very high dielectric constant might not be an advantage. In the case of terpolymers, this leads to early polarization saturation, i.e., polarization response saturates under an electric field much lower than the breakdown field and causes lower than expected energy density. Due to the dielectric nonlinearity and early saturation of polarization, the energy density of the terpolymers increases linearly with the applied electric fields. It was also found that the polymer-metal interface played an important role for conduction and the breakdown field in the terpolymers, which was related to the charge injection from the metal to the polymer.

Due to highly nonlinear dielectric behavior and early polarization saturation in the terpolymers, it was proposed that a high dielectric constant might not be desirable to obtain high energy density. Poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE), 10, 15 and 20 wt% CTFE) and Poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP), 10 and 12 wt% HFP) copolymers, which possess a much lower dielectric constant (about 12 at 1 kHz at room temperature), were further investigated for dielectric materials of high energy density. Due to the lower dielectric constant, the early polarization saturation was avoided and these polymers showed a very high breakdown field and energy density. For the P(VDF-CTFE) copolymer with 15 wt% CTFE, an energy density of higher than 24 J/cm³ at an electric field higher than 650 MV/m could be obtained. Based on thermal and microstructure studies, the high energy density was found to be caused by the structural modification of PVDF by bulky CTFE or HFP, which also act as defects, similar to the terpolymers. The discharge behavior of the copolymers
mainly relies on the load resistors, suggesting that the copolymers have lower equivalent series resistance.

Multi-component material system based on current available materials was found to be a useful strategy to tailor and improve the performance of dielectric materials. Nanocomposites composed of the P(VDF-TrFE-CFE) terpolymers and ZrO₂ or TiO₂ nanoparticles were found to greatly enhance the polarization response and energy density of terpolymers (from 9 J/cm³ to 10.5 J/cm³). Based on comprehensive thermal, dielectric and microstructure studies, the enhancement was believed to be related to the large amount of interfaces in the nanocomposites. In the interfaces, the chain mobility is increased and the energy barrier between the polar and nonpolar phases is reduced, resulting in higher polarization response and energy density at a reduced electric field.

The P(VDF-TrFE-CFE) terpolymer/P(VDF-CTFE) copolymer and the P(VDF-TrFE-CFE) terpolymer/PMMA blends were also studied. It was found that the P(VDF-TrFE-CFE) terpolymers could not be completely miscible with the P(VDF-CTFE) copolymer. In the P(VDF-TrFE-CFE) terpolymer/P(VDF-CTFE) copolymer blends, with a small amount of the copolymer (5 and 10 wt%) in the terpolymer, enhancement of the polarization response similar to that observed in the terpolymer/ZrO₂ nanocomposites was observed. This enhancement was also thought to be mainly caused by the interface effect. The breakdown field of blends was also greatly improved, which resulted in a significant improvement in energy density (from 9 J/cm³ to 11.5 J/cm³).

The P(VDF-TrFE-CFE) terpolymers are miscible with PMMA. Addition of PMMA was found to reduce the dielectric response of blends, but also to improve the breakdown field due to the improvement of mechanical properties. The optimum composition of the blends is around 2.5 wt% PMMA. With this composition, the breakdown field of the blends can be improved without reduction of energy density.
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Chapter 1

Research Background and Statement of Goals

At least three types of technologies were employed to store electrical energy including battery, capacitor, and inductor. Among them, capacitor technology is one of the most important technologies. Capacitors, as well as other passive components, occupy a very large volume (up to 70% in some cases) or weight in many electrical and electronic systems. The miniature of these systems, scaling-down of integrated circuits and the development of some new technologies (such as hybrid vehicles, implantable heart defibrillators) require capacitors with suitable dielectric properties, high energy density and high volume or weight efficiency.[1-4]

1.1 A brief summary of the capacitor technologies

The first capacitor was discovered in the 1740’s by Ewald Georg von Kleist and Pieter van Musschenbroek. The capacitor was named Lyden Jar, which was composed of a jar with metal electrodes inside and outside of the jar. The glass jar was the dielectric material in the prototype capacitor.[5] Nowadays, the basic structure of capacitors still takes the form of the Lyden Jar, as shown in Figure 1-1.[6] The parallel plate capacitor shown here is mainly composed of two layers of metal electrodes on the top and bottom of one layer of dielectric material, which can be ceramic or polymer or other dielectric materials. Besides this basic form of parallel plate capacitors, two types of capacitors, electrolytic and electrochemical capacitors, were also developed for some applications.[7]
Several important parameters are often employed to characterize a capacitor. The capacitance $C$ of a capacitor is used to evaluate the charge storage ability of the capacitor, which can be expressed as:

$$C = \frac{Q}{V}$$  \hspace{1cm} \text{(1.1)}

where $V$ is the applied voltage on the capacitor and $Q$ is the charge induced by the applied voltage. The stored electrical energy in the capacitor is:

$$U_{\text{store}} = \frac{1}{2} CV^2 = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} VQ$$  \hspace{1cm} \text{(1.2)}

The volumetric energy density $U_e$ of the capacitor can be calculated by dividing the $U_{\text{store}}$ with the volume of the capacitor.

In addition to these parameters, voltage rating and the temperature coefficient of capacitance are other important parameters to evaluate a capacitor.

### 1.1.1 Parallel plate capacitors

The basic structure of parallel plate capacitors is already presented in Figure 1-1. The performance of the capacitors is mainly determined by the dielectric materials. By measuring the capacitance $C$ of the parallel capacitor, the relative dielectric constant or
permittivity \( \varepsilon_r \), which is one of the intrinsic properties of the materials, can be calculated as follows:

\[
\varepsilon_r = \frac{Cd}{\varepsilon_0 A}
\]

where \( d \) is the thickness of the dielectric materials, \( A \) is the area of the capacitor; and \( \varepsilon_0 \) is the permittivity of the vacuum (\( \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \)).

For many applications, the energy density of dielectric materials is the most important factor rather than dielectric constant. In general, the volumetric energy density, which is a measure of the energy storage ability of a dielectric material, can be written as:

\[
U_v = \int_0^{D_{\text{max}}} EdD
\]

where \( E \) is the applied electric field on the dielectric materials, \( D \) is the electric displacement induced on the dielectric materials, and \( D_{\text{max}} \) is the maximum induced electric displacement.

Based on different polarization responses of dielectric materials under high electric fields, the dielectric materials can be divided into linear and nonlinear dielectric materials. Figure 1-2 shows the high field polarization responses of nonlinear and linear dielectric materials.[8] The shadowed area in the figure is the energy density of these materials during the discharge process. For nonlinear dielectric materials, the high field dielectric constant (the slope of the curve on the figure) will change with the electric field (Figure 1-2 (a), (b) and (d)); whereas the dielectric constant of linear dielectric materials is constant at all fields (Figure 1-2 (c)). The typical example for the materials with a polarization response shown in Figure 1-2 (a) is antiferroelectric material. The materials with a polarization response shown in Figure 1-2 (b) are ferroelectric materials. Figure 1-2 (d) shows the polarization response of the relaxor ferroelectric materials (at high temperature) or the ferroelectric materials in a paraelectric phase, in which no or very little hysteresis can be observed. It should be pointed out that the polarization response of the materials shown in Figure 1-2 (c) and (d) is the ideal case. In reality, these materials still have polarization-hysteresis-like dielectric response under high electric field due to...
the inevitable conduction loss, which will reduce the released energy density of these materials.

With the same electric field and the same polarization level, antiferroelectric materials possess much higher energy density than that of ferroelectric materials, as manifested by the shadowed area in the figure. For the ferroelectric materials, due to the remnant polarization ($P_r$), a large amount of energy is stored in materials rather than released. Therefore, $P_r$ has to be reduced to increase the discharge energy density of ferroelectric materials. For linear dielectric materials, because of their small dielectric constant, a very high field is required to reach the same polarization response and energy density as nonlinear materials.

In many published results, the energy density was calculated by the following equation simply using the weak-field dielectric constant $\varepsilon_r$ and breakdown electric field $E$:

$$U_e = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2$$  \hspace{1cm} 1.5

As will be shown in this thesis, Eq. 1.5 sometimes can be quite misleading due to the fact that the dielectric response of the materials with high energy density is normally nonlinear. Furthermore, the energy density loss can cause the significant deviation of the real energy density from the result calculated from Eq. 1.5.
Loss tangent \( \tan \delta \) is an indication of energy loss during the operation of dielectric materials, which can be expressed as the ratio of the imaginary part of permittivity \( \varepsilon'' \) to the real part of permittivity \( \varepsilon' \):

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]

Several types of dielectric materials are used to manufacture capacitors, including polymer film, ferroelectric and antiferroelectric ceramics, mica, impregnated paper, diamond-like carbon film, glass, glass ceramics and metal oxides with high breakdown fields. Here, a brief review of these dielectric materials will be presented.

### 1.1.1.1 Polymer dielectric materials

Polymers have been found to be a class of dielectric materials with high energy density. The common polymer-based dielectrics for capacitor manufacturing include polypropylene (PP), polyester (PET), Polyethylene naphlate (PEN), Polyphenylenesulfide (PPS), and Polyvinylidene fluoride (PVDF). Among them, biaxially orientated polypropylene (BOPP) is the most widely used polymer because of its high breakdown field, low cost and easy processing. The dielectric properties and performance of various polymer materials for capacitor applications are summarized in Table 1-1.[9-11]

**Table 1-1: Polymer materials for capacitor applications [10]**

<table>
<thead>
<tr>
<th>Plastic film</th>
<th>( \varepsilon' )</th>
<th>Maximum operating temperature ( ^\circ\text{C} )</th>
<th>Voltage Breakdown ( \text{V/\mu m} )</th>
<th>Dissipat. Factor % at 1kHz</th>
<th>Energy density ( \text{J/cc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (PP)</td>
<td>2.2</td>
<td>105</td>
<td>640</td>
<td>&lt;0.02</td>
<td>1.2</td>
</tr>
<tr>
<td>Polyester (PET)</td>
<td>3.3</td>
<td>125</td>
<td>570</td>
<td>&lt;0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td>2.8</td>
<td>125</td>
<td>528</td>
<td>&lt;0.15</td>
<td>0.5-1</td>
</tr>
<tr>
<td>Polyvinylidene- fluoridite (PVF)</td>
<td>12</td>
<td>125</td>
<td>590</td>
<td>&lt;1.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Polyethylene-naphlate (PEN)</td>
<td>3.2</td>
<td>125</td>
<td>550</td>
<td>&lt;0.15</td>
<td>1.5</td>
</tr>
<tr>
<td>Polyphenylenesulfide (PPS)</td>
<td>3.0</td>
<td>200</td>
<td>550</td>
<td>&lt;0.03</td>
<td>1.5</td>
</tr>
</tbody>
</table>
As shown in Table 1-1, the polymeric dielectric materials normally exhibit a very high breakdown field (>500 MV/m). Therefore, even though the dielectric constant of polymer materials is low, around 3, the energy density of the polymer is relatively high, as can be deduced from Eq. 1.5. PVDF possesses the highest dielectric constant among these polymers listed in Table 1-1, but because of its ferroelectricity and large remnant polarization, its energy density is not much higher than other polymers although its dielectric constant is about 4 times that of other polymers. Therefore, in order to improve the energy density of polymer dielectrics, polymers of high dielectric constant should be explored, but other factors such as polarization hysteresis and dielectric nonlinearity should also be considered.

One advantage of polymer-based capacitors over capacitors made from other dielectric materials is the self-healing phenomenon, which makes polymer film capacitors very reliable for applications under high electric fields.[11-14] The self-healing process is schematically illustrated in Figure 1-3. When the electrical breakdown occurs (in many cases around the defects in the polymers), the breakdown will result in the discharge of part of stored energy and the polymer film will be punctured by the released energy. At the same time, the metal electrode deposited on the surface of the polymer is quickly vaporized and driven outward from the breakdown site. After these processes, the polymer film will break down “open” rather than “short”. The whole capacitor system can still keep its function with only a little drop of capacitance.

![Figure 1-3: Schematic illustration of the process of self-healing in polymer dielectrics](image)
1.1.1.2 Ferroelectric and antiferroelectric ceramics

Due to the contribution of ferroelectric polarization, ferroelectric ceramics normally show very high dielectric constant. Table 1-2 shows the dielectric constant of conventional ferroelectric materials for capacitor applications, including (Ba,Sr)TiO$_3$, Pb(Zr,Ti)O$_3$ (PZT), and Pb(Mg,Nb)O$_3$-based ferroelectric relaxors.[15] The dielectric constant of these materials can be higher than 1000, much higher than polymer. It was reported that the dielectric constant of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ ceramics was about 30000.[16,17]

Table 1-2: The dielectric constant of typical ferroelectric ceramics and the comparison with non-ferroelectric inorganics [15]

<table>
<thead>
<tr>
<th>High-permittivity (perovskite) dielectrics</th>
<th>Low-permittivity dielectrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ba,Sr)TiO$_3$</td>
<td>SiN</td>
</tr>
<tr>
<td>$\varepsilon$=250-2000</td>
<td>$\varepsilon$=7-9</td>
</tr>
<tr>
<td>Pb(Zr,Ti)O$_3$</td>
<td>Diamond-like carbon</td>
</tr>
<tr>
<td>$\varepsilon$=400-4000</td>
<td>$\varepsilon$=4-5</td>
</tr>
<tr>
<td>Pb(Mg,Nb)O$_3$</td>
<td>Ta$_2$O$_5$</td>
</tr>
<tr>
<td>$\varepsilon$&gt;3000</td>
<td>$\varepsilon$=20-25</td>
</tr>
</tbody>
</table>

The multilayer ceramic capacitors, capacitors composed of hundreds of thin layers of ferroelectric ceramic film (thickness can be less than 3 $\mu$m), have very large volumetric capacitance, which can be comparable with electrolytic capacitors. Although the dielectric constant is very high, the breakdown field of ferroelectric ceramics is relatively low, as shown in Figure 1-4, the breakdown field of PZT-based ceramics.[15] The breakdown field of ferroelectric ceramic is normally less than 100 MV/m, in contrast to several hundreds MV/m of polymer dielectric materials. Also due to the highly nonlinear dielectric response of the ferroelectric ceramics (as shown in Figure 1-5, the dielectric constant decreases quickly with electric field in BaTiO$_3$ ceramics), the energy density of ferroelectric ceramics is not as high as expected.[18] Energy density of about 2 J/cm$^3$ has been reported. The energy density of commercial ceramic capacitors is only
around 0.01 J/g (less than 0.1 J/cm$^3$), much less than polymer-based materials, which is around 1 J/cm$^3$.[8,9]

Figure 1-4: The dielectric strength of PZT-based ferroelectric thin film [15]

Figure 1-5: Dielectric constant as a function of the temperature and the applied electric field of BaTiO$_3$ ferroelectric ceramics [18]
Anti-ferroelectric ceramics are another type of highly nonlinear dielectric materials. Unlike ferroelectric materials, under high electric fields, the dielectric constant of anti-ferroelectric increases with the electric field due to the phase transition between anti-ferroelectric and ferroelectric phases (Figure 1-2 (a)). It has been shown that an energy density of about $12 \text{ J/cm}^3$ can be obtained in antiferroelectric materials.[19-22] The energy density of some typical antiferroelectric ceramics is shown in Table 1-3 (PLZT is the abbreviation of (Pb, La)(Zr, Ti)O$_3$ ceramics).[22]

Table 1-3: Energy density of some typical antiferroelectric compositions [22]

<table>
<thead>
<tr>
<th>Composition</th>
<th>#</th>
<th>Applied field (kV/cm)</th>
<th>Energy on discharge (Joules/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLZT 2/95/5</td>
<td>5</td>
<td>150</td>
<td>$3.0 \pm 0.025$</td>
</tr>
<tr>
<td>PLZT 2/95/5</td>
<td>1</td>
<td>200</td>
<td>4.0</td>
</tr>
<tr>
<td>PLZT 2/95/5</td>
<td>1</td>
<td>320</td>
<td>4.0</td>
</tr>
<tr>
<td>PLZT 6/95/5</td>
<td>6</td>
<td>200</td>
<td>$2.76 \pm 0.44$</td>
</tr>
<tr>
<td>PLZT 6/95/5</td>
<td>5</td>
<td>260</td>
<td>$4.81 \pm 0.32$</td>
</tr>
<tr>
<td>PLZT 6/95/5</td>
<td>4</td>
<td>300</td>
<td>$6.05 \pm 0.57$</td>
</tr>
<tr>
<td>PLZT 8/95/5</td>
<td>5</td>
<td>200</td>
<td>$1.6 \pm 0.14$</td>
</tr>
<tr>
<td>PLZT 8/95/5</td>
<td>1</td>
<td>250</td>
<td>2.5</td>
</tr>
<tr>
<td>PLZT 8/95/5</td>
<td>1</td>
<td>265</td>
<td>4.6</td>
</tr>
<tr>
<td>PLZT 8/95/5</td>
<td>2</td>
<td>300</td>
<td>4.6</td>
</tr>
<tr>
<td>PLZT 8/95/5</td>
<td>1</td>
<td>350</td>
<td>5.5</td>
</tr>
<tr>
<td>PLZT 8/95/5</td>
<td>1</td>
<td>200</td>
<td>$1.1 \pm 0.1$</td>
</tr>
<tr>
<td>PLZT 8/95/5</td>
<td>1</td>
<td>250</td>
<td>1.7</td>
</tr>
<tr>
<td>PLZT 6/90/10</td>
<td>1</td>
<td>100</td>
<td>1.6</td>
</tr>
<tr>
<td>PLZT 6/90/10</td>
<td>1</td>
<td>200</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The ceramic capacitors do not show the self-healing ability, which is a serious reliability problem for the applications under high electric fields. Another significant limitation of ceramic capacitors is the size limitation (ceramics are difficult to make into large capacitors) due to the stress induced catastrophic failure. Also, for ceramic capacitor of large size, binder burn-out during the ceramic processing is another problem.
1.1.1.3 Glasses and glass ceramics

Quite similar to the polymer-based materials, some glass materials have a very high breakdown field (as high as 1 GV/m), but the dielectric constant of the materials is relatively low (most of them below 10). [23] One advantage of the glass materials is their good temperature stability of the performance. In order to further improve the dielectric properties, glass-ceramics, which are comprised of a glass matrix and ferroelectric ceramic particle/grain constituent, was proposed.[24-27] It was expected that the energy density of glass-ceramics could be as high as 6-8 J/cm³ because they combined the merits of a high breakdown field of glass and a high dielectric response of ferroelectric ceramics in one material. Probably due to the interfacial effect, an experimental result shows that the measured energy density is much lower than the expected value (0.3-0.9 J/cm³).[27,28] The typical glass-ceramic systems investigated for capacitor applications are PbO-BaO-SrO-Nb₂O₅-B₂O₃-SiO₂, Na₂O-PbO-Nb₂O₅-SiO₂ and BaO-TiO₂-Al₂O₃-SiO₂.

1.1.1.4 Diamond and diamond-like carbon film

Diamond is known to have very good mechanical and thermal properties. The dielectric constant of a natural diamond is around 5.8 with a very high breakdown field (up to 2 GV/m). Therefore, very high energy density can be expected. Diamond film and diamond-like carbon, a mixture of carbon and hydrogen, can be prepared by chemical vapor deposition.[29-31] The dielectric constant of these materials can vary from 3.5 to 5.8 depending on the deposition conditions. One advantage of this type of material is the possibly good performance at high temperatures. The preparation of diamonds and diamond-like film needs substrate and the whole packaged energy density may be greatly reduced by the substrate.
1.1.1.5 Metal oxides

Several metal oxides (Al$_2$O$_3$, ZrO$_2$, Ta$_2$O$_5$, Nb$_2$O$_5$, TiO$_2$ etc.) with dielectric constants between 3 and 100 have been investigated for the possible applications as gate dielectric and high energy density capacitors.[32-36] Magnetron sputtering deposition method was developed to make thin film oxides of high quality.[32-33] The oxide thin film shows a very high dielectric breakdown field, depending on the dielectric constant, ranging from several MV/m to about 1 GV/m. Although these dielectrics have been predicted to have an energy density above 20 J/cm$^3$, in reality, due to the energy loss and nonlinear effect, the energy density of materials may not be that high. This type of material also lacks a self-healing ability for high electric field applications, which may be a serious reliability problem.

1.1.1.6 Other dielectric materials

Mica, dielectric fluid impregnated paper and vacuum have been used as dielectric materials for very long time.[9,37] Mica capacitor is known for its excellent temperature and chemical stability. The energy density of the mica capacitor is around 0.005 J/g. The paper capacitors have been in use for about one century and the energy density is about 0.4 J/g. Due to the low dielectric constant of vacuum, vacuum is not a good candidate dielectric for high energy density capacitor applications.

1.1.1.7 The ultimate energy density of dielectric materials and future’s exploration

The energy density of parallel-plate-type capacitors depends on the dielectric constant and the breakdown field of the dielectric materials, as already shown in Eq. 1.4 and Eq. 1.5.[38,39] By summarizing the dielectric constant and the breakdown fields of a variety of dielectric materials, as shown in Figure 1-6, it is found that the breakdown field
of dielectric materials decreases with increasing dielectric constant. The proposed relationship between the dielectric constant and the breakdown field is:

\[ E_b \propto (\varepsilon)^{\frac{1}{2}} \text{ or } E_b \propto (\varepsilon)^{-0.65} \text{ (for time dependent dielectric breakdown field)} \]  \( \text{1.7} \)

where \( E_b \) is the dielectric breakdown field and \( \varepsilon \) is the dielectric constant of the dielectric materials. The above relationship was explained by considering the local electric field and bond strength of the dielectric materials. This relationship implies that an ultimate energy density exists for the dielectric materials in nature.

For dielectric materials with a very low dielectric constant (\( \varepsilon < 5 \)), although their breakdown fields are very high, it is difficult for them to achieve high energy density. For example, the dielectric constant of \( \text{SiO}_2 \) is about 4. By using Eq. 1.5, we can estimate that an electric field of about 1 GV/m is required to obtain an energy density of 20 J/cm\(^3\). Even if \( \text{SiO}_2 \) can sustain such a high electric field, due to the significant conduction loss under a high electric field, the energy density will be below 20 J/cm\(^3\).

For dielectric materials with very high dielectric constants, such as ferroelectric ceramics, it is also difficult to obtain high energy density because the breakdown fields of these materials are low, as seen from Eq. 1.7 and Figure 1-6. We can take a data point

![Figure 1-6: A summary of the dielectric constant and dielectric strength of the common dielectric materials and their correlation.][38]
from Figure 1-6 as an example. The dielectric constant of PZT ceramic is about 1000 and its breakdown field is 80 MV/m. Even if the material is a linear dielectric material without loss, the maximum energy density calculated from Eq. 1.5 is about 28 J/cm$^3$. In reality, due to polarization hysteresis and the nonlinear polarization response of ferroelectric materials, as shown in Figure 1-2, the energy density is much lower than this value. Also, considering highly nonlinear conduction loss due to the polarization-related structure change under a high field, the energy density will be further reduced. As mentioned above, an energy density of only 2 J/cm$^3$ was measured in the ferroelectric ceramics.

Based on the above considerations, dielectric materials with an intermediate dielectric constant are promising to obtain high energy density. As will be shown in the thesis, for PVDF-based polymers with intermediate dielectric constant ($\sim$12) and high breakdown fields (higher than 600 MV/m), an energy density higher than 24 J/cm$^3$ can be achieved.

Polymeric antiferroelectric materials, which possess a lower dielectric constant than antiferroelectric ceramics, are another group of promising dielectrics with high energy density. However, very few polymers exhibit antiferroelectric properties. The copolymer of Ethylenetetrafluoroethylene (ETFE) is a possible antiferroelectric polymer. From our preliminary results, the polymer shows some signs of polarization switching typical of antiferroelectric materials, but it requires a very high electric field. Composition modification of the polymer is required to make the switching possible under a reasonable field.

As already summarized, a variety of materials have been studied for high energy density capacitor applications. Table 1-4, a table drawn in 1998, shows the highest energy density at that time and the possible future energy density of different capacitor technologies.[40] The polymer-based capacitors not only possess the highest energy density among these capacitor technologies, but also the highest projection energy density. Besides the high energy density, compared with other dielectric materials described above, polymer-based capacitors possess the ability of self-healing, which greatly improves the reliability of the capacitors. To further increase the energy density of
the dielectric materials in the future, polymer materials with reasonably large dielectric constant, high dielectric strength, and good temperature stability will be explored.

1.1.2 Electrolytic capacitors

Analogous to conventional parallel-plate-type capacitors, in the electrolytic capacitor, the charge or energy is also stored on a layer of dielectric materials. This layer of dielectric material is very thin and the surface of the dielectric material is rough, leading to a very large surface area. Therefore, compared with most parallel-plate-type capacitors, the electrolytic capacitors possess a very high capacitance due to their thinness and large surface area (the capacitance ranges 1-10^5 µF). Unlike the parallel-

Table 1-4: Comparison of various capacitor technologies [40]

<table>
<thead>
<tr>
<th>Capacitor System</th>
<th>kJ/kg Now / Future</th>
<th>kW/kg (average power) Now / Future</th>
<th>Rep-Rate Hz</th>
<th>Main Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Film</td>
<td>0.4 / 20</td>
<td>5 / 20 k</td>
<td>&gt; 100 k</td>
<td>* New Polymer Films</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Impregnants</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Foils and Conductors</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* &gt; 200 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* =&gt; 1 kJ/µF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Voltage Reversal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Pulse Duration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Repetition Rate</td>
</tr>
<tr>
<td>Ceramic</td>
<td>0.01 / 5</td>
<td>10 / 10 k</td>
<td>&gt; 1000 k</td>
<td>* Ceramic Formulations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Electrodes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* &gt; 300 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* 1 kJ/µF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Voltage Scaling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Fusing</td>
</tr>
<tr>
<td>Electrolytic</td>
<td>0.2 / 2</td>
<td>2 / 10 k</td>
<td>&gt; 10 k</td>
<td>* Electrolytes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Separators</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* &gt; 200 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* 1 kJ/µF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Gassing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Hermetic Sealing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Voltage Reversal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Pulse Repetition Rate</td>
</tr>
<tr>
<td>Mica</td>
<td>0.005 / 0.05</td>
<td>5 / 50 k</td>
<td>&gt; 100 MHz</td>
<td>* Electrodes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* &gt; 400 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* 1 kJ/µF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Voltage Scaling/Reversal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Impregnants</td>
</tr>
</tbody>
</table>

1.1.2 Electrolytic capacitors

Analogous to conventional parallel-plate-type capacitors, in the electrolytic capacitor, the charge or energy is also stored on a layer of dielectric materials. This layer of dielectric material is very thin and the surface of the dielectric material is rough, leading to a very large surface area. Therefore, compared with most parallel-plate-type capacitors, the electrolytic capacitors possess a very high capacitance due to their thinness and large surface area (the capacitance ranges 1-10^5 µF). Unlike the parallel-
plate-type capacitors, one or two electrodes of electrolytic capacitors are liquid or solid electrolyte.[7,41]

Figure 1-7 shows the construction of an electrolytic capacitor. The capacitor is comprised of a cathode, an anode, and paper for absorbing electrolyte. During the construction of an electrolytic capacitor, a thin layer of metal oxide is formed on the anode through electrochemical process. Because of this electrochemical process, the electrolytic capacitor normally has polarity and, in most cases, it is only used for DC applications.

Figure 1-7: The construction of an electrolytic capacitor [41]

The commercial electrolytic capacitors include several varieties, and the most common ones are aluminum and tantalum electrolytic capacitors, in which aluminum oxide and tantalum oxide are dielectric materials, respectively. Compared with an aluminum capacitor, a tantalum capacitor shows lower capacitance and energy density, but a more stable performance. A tantalum capacitor uses solid phase MnO₂ as electrolyte, which has no electrolyte leakage and less environmental problems, in contrast to the corrosive liquid electrolyte in aluminum capacitors.[42,43] In recent years, Aluminum electrolytic capacitors with solid electrolyte were also developed. Unlike tantalum capacitors, in aluminum capacitors, organic solid electrolytes, such as polypyrrole and semiconductor salt, are used.[7] One advantage of the electrolytic capacitors is their high volume capacitance. [16] Electrolytic capacitors have the ability
of self-healing, which is another advantage of this type of capacitor. This type of capacitor has moderate energy density, as shown in Table 1-4.

### 1.1.3 Electrochemical Capacitor

Besides the conventional parallel-plate-type and electrolytic capacitors, another type of capacitors, the electrochemical capacitors, have been intensively studied. This type of capacitors often has a very high capacitance, from several to hundreds of farads, in contrast to microfarads and millifarads of the capacitance of the normal parallel-plate-type capacitors. The electrochemical capacitors can be divided into two subcategories, based on the mechanisms of energy storage: double-layer capacitors and supercapacitors or ultracapacitors.

The double-layer capacitor was introduced as early as 1957 by Becker. After that, the double-layer capacitor was commercialized in 1969. The structure of a typical double-layer capacitor is shown in Figure 1-8.[44,45] It consists of a porous carbon electrode with a high surface area, electrolyte, and electrolyte separator.

![Figure 1-8: A schematic diagram of a double-layer capacitor](image)

Figure 1-8: A schematic diagram of a double-layer capacitor [44]
The origin of the high capacitance of the double layer capacitor comes from the double layer interfacial charge between carbon electrode and electrolyte, as shown in the figure. Therefore, the large surface area electrode is the key to improve the capacitance of the double layer capacitor. The calculated specific capacitance (capacitance per unit volume or mass) can be as high as 150-300 F/g, but in reality this value is below 200 F/g. The reason for this phenomenon is that not all the pores of the porous electrode can be accessed by the electrolyte, which reduces the efficiency of the porous electrode.[46]

Another type of electrochemical capacitors, which use pseudo-capacitance, are called supercapacitors or ultracapacitors.[47,48] The construction of this type of capacitor is similar to the double-layer capacitors. The electrodes of supercapacitors utilize specially treated carbon or, some kinds of metal oxides, such as RuO₂, or conductive polymer. The operation mechanism of this type of capacitor is closer to that of a battery. While charging, a faradaic process takes place, either by absorption of ions from the electrolytes, or by the redox reaction between electrolytes and electrodes, or by doping or undoping of conductive polymer, which is quite different from the double-layer capacitors mentioned above. The common supercapacitors using RuO₂ electrodes were taken as an example. During the charging and discharging processes, the following reaction is believed to happen:[48]

\[
\text{RuO}_2 + \delta \text{H}^+ + \delta \text{e}^- = \text{RuO}_2\cdot\delta(\text{OH})_\text{total}, \quad 0 \leq \delta \leq 2
\]

The capacitance of the supercapacitor is voltage dependent. The average capacitance of capacitor \( C_{av} \) is often calculated as:

\[
C_{av} = \frac{Q_{\text{total}}}{V_{\text{total}}}
\]

where \( Q_{\text{total}} \) and \( V_{\text{total}} \) are the total charge and voltage of the capacitors, respectively. Compared with double-layer capacitor, the supercapacitor normally has higher capacitance per unit volume and energy density, but larger RC constant (lower power density), than the double layer capacitor.

Table 1-5 summarizes the energy density and power density of current and future electrochemical capacitors.[45] The energy density of state-of-the-art electrochemical capacitor is around 10-20 J/g (carbon/organic) and an expected energy density of 30-40
J/g will be obtained in this type of technology. For electrochemical capacitor, the density is about 1-2g/cm³. [49] A weight energy density of 10-20J/g is corresponding to a volumetric energy density of 5-20J/cm³.

Table 1-5: Performance of state-of-the-art and future projections of the electrochemical capacitors [45]

<table>
<thead>
<tr>
<th>Type</th>
<th>Electrode/electrolyte</th>
<th>Present status</th>
<th>Future projections</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>WJ/kg</td>
<td>kW/kg</td>
</tr>
<tr>
<td>Double-layer</td>
<td>Carbon/aqueous</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>carbon/organic</td>
<td>5-6</td>
<td>0.5</td>
</tr>
<tr>
<td>Pseudo-capacitors</td>
<td>Anolyte/RuO₂/aqueous</td>
<td>0.6</td>
<td>0.5-2.0</td>
</tr>
<tr>
<td></td>
<td>hydrous RuO₂/aqueous</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>mixed metal oxide/aqueous</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>doped metal oxide/organic</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>doped conducting polymer/organic</td>
<td>1.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Carbon/NaIO₄/aqueous</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>carbon/NaIO₄/aqueous</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

1.1.4 Comparison of three types of capacitor technologies

Among the three technologies, the volumetric capacitance and energy density decrease in the order of electrochemical, electrolytic, and parallel-plate-type capacitors. The discharge speed, which is a determinant factor of power density and an important parameter for pulse power applications, increases in that order. Figure 1-9 summarizes the energy density, power density and discharge time of various energy storage technologies. As seen from the figure and Table 1-5, electrochemical capacitors possess the highest energy density among these capacitor technologies, but the lowest energy discharge time and power density. [40] On the other hand, parallel-plate-type capacitors show the highest discharge speed and power density, but their energy density is not high at present.
For solid state capacitors, the highest energy density of commercial capacitors is around 2.4 J/cm$^3$ (about 1.2 J/g, PVDF capacitors). For future development, if the energy density of parallel-plate-type capacitors can be 20 J/g (about 5-20 J/cm$^3$), which is energy density obtained by electrochemical capacitors, they can compete with the electrochemical capacitors, also considering the high power density of the parallel-plate-type capacitors. Although some dielectric materials, such as metal oxides and diamond-like materials, may reach such a level of energy density, the polymer-based materials are the promising ones because the polymer materials can be used under high electric field with high reliability due to their ability of self-healing. Also, polymer-based film capacitors are easy to fabricate and suitable for capacitors with larger sizes. The problem of current polymer dielectric materials is their low dielectric constant. Therefore, how to improve the dielectric constant of polymer materials with a high dielectric breakdown field is an issue for the development of high energy density capacitors, which is the main objective of this thesis.

Figure 1-9: Energy density, discharge speed, and power density of various technologies for the electrical energy storage. [40]
1.2 Development of PVDF-based polymers with high dielectric constant

For most polymers, as shown in Table 1-1, the dielectric constant is too low to further improve the energy density by improving the breakdown field. Dielectric polymers with a high dielectric constant are needed to reach a higher energy density. PVDF-based polymers, which are a class of ferroelectric materials, possess a relatively high dielectric constant and breakdown field, indicating a possible high energy density in this class of materials. The ferroelectricity of PVDF originates from the relatively large switchable (by electric field) dipole moment of fluorocarbons in the polymer chain. The dipole moment of C-F bond is about 2.1 Debye (1 Debye is $3.34 \times 10^{-30}\text{C.m}$). [50]

PVDF-based polymers are semicrystalline polymers. The crystalline phases have at least four polymorphs, as summarized in Lovinger’s paper. [50] Figure 1-10 shows chain conformations of TG, all-trans and T$_3$G and Figure 1-11 illustrates four types of polymorphs, which are named $\alpha$ (form II), $\beta$ (form I), $\gamma$ (form III), and $\delta$ (form $\Pi_p$). Among them, $\alpha$ and $\beta$ phases are the most studied polymorphs. [51]

![Figure 1-10: Three types of chain conformations for PVDF-based polymer](image-url)
The polymer chains of α phase are in the trans-gauche-trans-gauche’ (GTGT) conformation. α phase has orthorhombic symmetry with unit cell dimension of a=4.96 Å, b=9.64 Å and c=4.62 Å.[52] It has a dipole moment perpendicular to the polymer chain. Due to the opposite orientation of the neighboring chains, the total dipole moment in one unit cell is zero. Therefore, α phase is the so-called non-polar phase of PVDF. δ phase is the polar polymorph of α phase. By applying an electric field on PVDF with α phase, the dipoles of neighboring chains can be aligned to the same orientation. Net dipole moment is generated and α phase is transformed into δ phase.

β phase and γ phase are two polar polymorphs of PVDF. For more than thirty years, β phase PVDF has been extensively studied for piezoelectric and pyroelectric applications. β phase PVDF is also in orthorhombic symmetry and the unit cell size is a=8.58 Å, b=4.90 Å, and c=2.56 Å.[53] The polymer chain of β phase has all-trans (TT) conformation in which the dipoles point to the same direction resulting in the highest possible dipole density among the four polymorphs. For γ phase, on the other hand, the polymer chain has TTGTGTG conformation.

By a common preparation method, such as solution cast or compression molding, α phase PVDF is normally obtained at room temperature. α phase can be further
transformed into β phase by stretching. The interconversion between the polymorphs by different processing is shown in Figure 1-12.[51]

For PVDF homopolymer, although typical polarization-electric field hysteresis can be observed (an indication of ferroelectricity), it lacks evidence of Curie temperature, another indication of ferroelectricity, which raised the controversy of whether PVDF is a ferroelectric material. Experimental results on copolymer of VDF and trifluoroethylene (TrFE) suggested that the Curie temperature of PVDF homopolymer was higher than its melting temperature and could not be observed even when PVDF melted. Incorporation of TrFE into the PVDF polymer chain reduces the Curie temperature to a temperature below melting temperature. Figure 1-13 shows the phase diagram between VDF and TrFE. Copolymers with 50-80 mol% VDF show the Curie temperature below their melting temperature.[54]
PVDF and its copolymers have a relatively large dielectric constant (>10) and a high breakdown field, indicating a possible high energy density in these groups of materials. However, due to the very large polarization hysteresis of PVDF homopolymer and its copolymer, as shown in Figure 1-14, the bipolar P-E loops of P(VDF-TrFE) copolymer, although the polarization response of these polymers is very high, the discharged energy (the shadowed area in the figure) is only a small portion of the stored energy.

Figure 1-13: Phase diagram of P(VDF-TrFE) copolymers.[54]

Figure 1-14: The polarization response under a high field for PVDF-based copolymers (normal ferroelectric) and terpolymers (relaxor ferroelectric). The shadow areas show the energy density of these materials.
energy. Therefore, it is obvious that by reduction of the polarization hysteresis, the energy density of PVDF-based polymers can be further improved.

Figure 1-15 shows the effect of electron irradiation on the polarization hysteresis of P(VDF-TrFE) copolymer.[55,56] With increasing irradiation dosage, the remnant polarization was gradually reduced; and a higher discharge energy density can be expected in the irradiated copolymer.

![Polarization vs Electric Field](image)

Figure 1-15: Dependence of bipolar P-E loops on electron irradiation dosage. The remnant polarization of irradiated copolymers decreases with increasing irradiation dosage. [56]

The weak field dielectric properties of irradiated copolymer exhibit the dielectric behavior of relaxor ferroelectric, which was observed for the first time in the polymers, as shown Figure 1-16. The temperature, at which the dielectric constant reaches its maximum, shifts to lower temperature, resulting in large dielectric constant at room temperature (larger than 50 at 1kHz), in contrast to about 3 for nonpolar polymers and around 15 for non-irradiated copolymer. The break-up of a coherent polarization response of ferroelectric domains in P(VDF-TrFE) copolymers by the introduction of defects into the polymer chain through electron irradiation is the main reason for the conversion from normal ferroelectric properties of P(VDF-TrFE) copolymers to relaxor ferroelectric behavior of irradiated copolymers. As illustrated in Table 1-6, decrease of the ferroelectric domain size with irradiation dosage was observed by XRD.[57] When the irradiation dosage was higher than 65 Mrad, no macro ferroelectric domains could be
detected and macro-domains were converted into unstable local polar regions. Accompanying this process, an increasing amount of the TG and T₃G conformations at the expense of the all-trans conformation with increasing irradiation dosage was observed by FT-IR.[56]

Table 1-6: Change of domain size and crystal size with irradiation dosage [57]

<table>
<thead>
<tr>
<th>Dose (Mrad)</th>
<th>Lp (nm, Paral)</th>
<th>Lp (nm, Perp)</th>
<th>Lc (nm, Paral)</th>
<th>Lc (nm,Perp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.5</td>
<td>7.5</td>
<td>35</td>
<td>&gt;7.5</td>
</tr>
<tr>
<td>10</td>
<td>7.5</td>
<td>7.1</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5.8</td>
<td>7.05</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>5.7</td>
<td>5.0</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.83</td>
<td>2.5</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td>35</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td></td>
<td>35</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>18</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lp: polar domain size, Lc: crystallite size or coherence X-ray scattering domain size (for dose higher than 65 Mrads)

Figure 1-16: Temperature dependence of dielectric property of electron irradiated copolymers.[55]
Although irradiated copolymers show good dielectric and electromechanical properties, the irradiation process is costly and not convenient. Therefore, other method to introduce defects into the copolymers was studied. It was found that copolymerization of bulky termonomers, such as CFE (chlorofluoroethylene) and CTFE (chlorotrifluoroethylene), with P(VDF-TrFE), could also effectively convert the P(VDF-TrFE) copolymers from normal ferroelectric to relaxor ferroelectric.[58-60] CFE and CTFE, which have large chlorine atom, act as defects in crystal lattice, and break up the ferroelectric domains into local nano-polar regions. As a result, similar to irradiated copolymers, P(VDF-TrFE)-based terpolymers also exhibit relaxor ferroelectric behavior and a high dielectric constant (about 50) at room temperature, as shown in Figure 1-17, the temperature dependence of the dielectric constant of a terpolymer. The high field polarization response of terpolymer can be found on Figure 1-14. The shadowed area, which is the discharge energy density of terpolymer, is much larger than copolymer, suggesting a significant effect of defect modification on the dielectric properties of copolymers. In Chapter 2, the applications of P(VDF-TrFE-CFE) terpolymers for high energy density capacitors will be investigated in detail.

Figure 1-17: Temperature dependence of dielectric constant of P(VDF-TrFE-CFE) terpolymer.[59]
1.3 Polymer-based composite materials

As mentioned above, polymer-based materials normally have a relatively low dielectric constant. Besides the exploration of new materials with high dielectric properties, another approach to improve the dielectric constant of polymer is to mix with another component with a high dielectric constant, normally ferroelectric ceramic particles. However, incorporation of micro-sized ceramic particles can also significantly reduce the breakdown field and can not gain much in the energy density. In recent years, the concept of nanodielectrics was proposed.\cite{61,62} It was proposed that by adding nanoparticles into the polymer could not only improve the dielectric constant of composites, the breakdown field could be also improved due to interface effect in the nanocomposite.\cite{63-66} Therefore, the energy density could probably be improved in the nanocomposites.

1.3.1 Improvement of the dielectric constant by composite method

One straightforward way to improve the dielectric constant of a polymer is the addition of high dielectric constant materials. Normally, ferroelectric ceramics, such as BaTiO$_3$, Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$-PbTiO$_3$ (PMN-PT) or other ferroelectrics or relaxor ferroelectrics, possess a very large dielectric constant, as already shown above. Studies have shown that the high dielectric constant ceramic fillers could greatly increase the dielectric properties of a composite.\cite{67,68} For example, irradiated P(VDF-TrFE) copolymer/PMN-PT composites were found to exhibit a dielectric constant as high as 250, as shown in Figure 1-18.\cite{67} The breakdown field of this composite system was 120 MV/m. Therefore, a relatively high energy density was expected in the composites. The disadvantage of the conventional polymer/ceramic composite with micro-sized filler is that a very high volume percentage of ceramic loading is required to improve the dielectric properties significantly. At such a high volume percentage, the mechanical properties of the composite will deteriorate. At the same time, the breakdown field of
composite materials will also be greatly reduced. Therefore, the energy density can not be improved much through this method.

Another strategy to improve the dielectric constant of the polymer is to add conductive or semiconductive fillers in the insulator matrix.[69-72] It is known that for polymer/conductive filler composites, the dielectric constant of a composite can be greatly improved at a threshold volume fraction \( f_c \) (percolation threshold), which can be described by the equation below:

\[
\frac{\varepsilon}{\varepsilon_m} \propto |f_c - f|^\delta
\]  

where \( \varepsilon \) and \( \varepsilon_m \) are the dielectric constant of composite and matrix respectively, and \( f \) is the volume fraction of fillers. By this strategy, the dielectric constant of composites can be increased to tens or even hundreds times the polymer matrix. For example, in the Cu-Pc/PANI/PU system, the dielectric constant can be as high as 800.[70]

Many studies in this area were concentrated on polymer/metal composites. Similarly, the dielectric constant of about 400 can be obtained in the polymer/metal composites.[71] One serious problem for these composites is the increase of dielectric loss simultaneously with the dielectric constant. When the compositions of composites approach the percolation threshold, the dielectric loss is normally very high and the breakdown field is also reduced. Recently, it was reported that by coating the metal
particles with a layer of carbonaceous shell, the dielectric loss of epoxy/Ag nanocomposites could be greatly reduced ($\tan\delta$ below 10%) and the dielectric constant could still be as high as 100.[72] At present, the dielectric strength of this class of materials is not clear. Therefore, the usefulness of composites composed of polymer and conductive or semiconductive fillers for high energy density capacitor applications requires further study.

1.3.2 Improvement of the breakdown field and other high field properties in nanocomposites

The advantage of nanocomposites over conventional microcomposites has been proved by the improvement of mechanical properties of the polymer matrix due to a large ratio of surface to volume of nanoparticles and a significant amount of interfacial regions between nano-sized fillers and polymer matrix. In recent years, it was proposed that nanofillers could improve the electrical and dielectric properties of the polymers based on the assumption that a large amount of interfaces may have beneficial effects on these properties. Experimental results have demonstrated that only a small amount of nanofillers (normally less than 10 wt%) could increase the breakdown field, improve the resistance of partial discharge, and mitigate the internal space charge accumulation, which could improve the energy density and high field performance of the polymer materials.[63-66,73]

Because of the significant effect of interface between polymer and nanoparticle on the dielectric performance of the nanocomposite, it is very important to understand the nature of interface in the nanocomposite. T. J. Lewis proposed a double layer model to explain the interface in the nanocomposites. [74] Figure 1-19 schematically shows the interface between the nanoparticle and polymer. For several reasons, such as charge injection, nanoparticles may take a certain amount of charge on the surface of particles. The surface charge then forms a charge distribution layer called Gouy-Chapman diffuse layer in the polymer.
Another model proposed by T. Tanaka, et al., suggested, in addition to the electric double layer, there was a three-layer structure, which was overlapped by the electric double layer, as shown in Figure 1-20.[75] The three-layer structure consists of a bonded layer, which is a transitional layer tightly bonded with polymer and nanoparticle, a bound

Figure 1-19: Illustration of the double-layer model for the interfaces in the nanocomposites [74]

Figure 1-20: Multi-core model for nanoparticle-polymer interface in the nanocomposites [75]
layer about 2-9 nm, which is formed by a polymer chain strongly bound to the first layer, and a third loose layer, which is a region loosely coupling the second layer. By using this model, the authors could explain the improvement of partial discharge resistance in nanocomposites.

It was found that interface layers in the nanocomposite might be more conductive than the polymer matrix, which mitigated the space charge accumulation and field concentration by fast charge dissipation. Reduction of internal charge accumulation, combined with other effects, such as electron scattering, reduction of free volume, the breakdown field of nanocomposites was found to be higher than neat polymer in several reports. Therefore it is possible to improve the energy density of polymer by nanocomposite strategy.

How to prepare nanocomposites with well-dispersed nanoparticles is a very important issue. The surface state of nanoparticles can greatly affect the dispersion of nanoparticles and ultimate properties of nanocomposites [76,77].

1.4 Statement of goals

Various capacitor technologies have been summarized in this chapter. Among them, the polymer film capacitors possess a relatively high energy density, high power density, fast discharge speed and low loss, which make them very useful for the energy storage and pulse power applications. Compared with the electrochemical capacitors, which exhibit the highest energy density among these capacitor technologies, the energy density of the polymer film capacitors is relatively low. Therefore, the goal of the work is to explore and develop polymer-based dielectric materials of high dielectric energy density. For this final goal, PVDF-based polymers, nanocomposites and blends were investigated in this work. This work can be divided into the following categories:

1. PVDF-based terpolymers have been developed in our group, which show a high dielectric constant and excellent electromechanical properties. The applications of terpolymers for dielectric materials of high energy density will be further evaluated in this work. Parameters and issues related to capacitor applications, including the weak
field and high field dielectric properties, dielectric nonlinearity, discharge speed, dielectric strength, and charge injection, will be studied in the second chapters.

2. High dielectric constant does not necessarily result in high energy density. The relationship between dielectric constant, breakdown field and energy density will be analyzed in the third chapter. Polymers with a suitable dielectric constant and high breakdown field will have higher energy density. Based on this understanding, PVDF-based copolymers, which have a reasonably high dielectric constant, will be investigated. The relationship of compositions-structure-properties in these copolymers will also be studied. This work, combined with the results of the terpolymers, may provide insight into the composition design for polymers with high energy density.

3. Besides the exploration of new polymer materials, starting from the current available materials, composite is another strategy to design materials of high energy density. In the fourth and fifth chapters, PVDF-based polymer blends and nanocomposites will be investigated. The efforts will be focused mainly on two aspects. The first is how polymer or ceramic fillers affect the microstructure, dielectric properties and energy density of the polymer matrix. The effort will also be concentrated on the contribution of interfaces to property improvement and the mechanisms for this improvement in these multi-component systems. Hopefully, the studies will contribute to understanding the interfaces in the nanodielectrics.
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[57] Q. M. Zhang, Talk in Pittsburgh


Chapter 2

Investigation of the PVDF-based Terpolymers for High Energy Density Capacitor Applications

As described in the proceeding chapter, poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) terpolymers possess a very high dielectric constant (>50) at room temperature, the highest among the known dielectric polymers. It has been demonstrated that P(VDF-TrFE-CFE) terpolymers exhibit excellent electromechanical properties.[1,2] The high dielectric constant and slim polarization hysteresis suggest the PVDF-based terpolymers as candidate materials to achieve high energy density. In this chapter, the properties pertinent to the high energy density capacitor applications of the terpolymers, including the microstructure, the weak-field and high-field dielectric properties are characterized systematically. Other issues, such as charge injecting and interface effect, which are very important for high field applications, will also be discussed here.

2.1 Experimental

P(VDF-TrFE-CFE) terpolymer was synthesized via a suspension polymerization process.[3] The compositions of terpolymers are denoted as VDF/TrFE/CFE x/(1-x)/y, in which the x/(1-x) reflects the molar ratio of VDF to TrFE and y is the molar percentage of CFE in the terpolymer composition. The following compositions of terpolymers were studied: VDF/TrFE/CFE 70/30/8.1, 63/37/7.5, 65/35/4 and 64/36/7.2. The terpolymer films used in the investigation were fabricated using the solution cast and compression molding methods. In the solution cast method, the terpolymer powder was dissolved in N,N-Dimethylformamide (DMF); the terpolymer solution was then poured on clean glass slides and dried at 70-80°C. After casting the films were annealed at 120°C for more than 2 hrs. to remove residual solvent and to raise the crystallinity. The typical film thickness
in this investigation is between 10 µm and 20 µm. For the purposes of comparison, P(VDF-TrFE) (65/35) copolymer film was also prepared by solution cast method. The preparation procedure is the same as for the terpolymer, and the only difference is that the annealing temperature of the copolymer is 130ºC. For some measurements, such as dynamic mechanical analysis (DMA), thicker film was needed (40 µm or thicker film was used). The thick film was prepared by compression molding at 230ºC for 5-10 min.

For electrical testing, gold and silver electrodes were deposited on the surface of terpolymer film by the sputtering method, and aluminum was deposited using thermal evaporation. The weak field dielectric properties were measured by a multi-frequency LCR meter (HP4284). Temperature dependence of the weak field dielectric properties were measured by a characterization system comprised of a LCR meter (HP4284), a furnace (Delta 9023) and a computer for temperature control and data collection. The bipolar and unipolar electric displacement-electric field (D-E or P-E loops) curves were measured by a modified Sawyer-Tower circuit. The dielectric energy density of the terpolymer was calculated from the unipolar P-E loops. The breakdown electric field was measured by applying a linearly increasing voltage (ramp rate is 500 V/m) on the terpolymer film. The electrode size of the samples for the breakdown test was 2.45 mm. Typically, 10-15 samples were tested and the breakdown electric fields were analyzed by Weibull analysis.

The surface morphology of polymer film was studied by Scanning Electron Microscopy (SEM, Hitachi S-3000H). The molecular conformations were characterized by Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 510).
2.2 Experimental results and discussions

2.2.1 Change of dielectric properties from the P(VDF-TrFE) copolymer to the P(VDF-TrFE-CFE) terpolymer

Figure 2-1 shows the curves of weak field dielectric properties vs. temperature $T$ of the P(VDF-TrFE) (65/35) copolymer and the P(VDF-TrFE-CFE) terpolymer (63/37/7.5). With increasing temperature, the dielectric constant $\varepsilon$ of the copolymer increases and reaches its maximum at a temperature of about 92°C, which is the Curie temperature ($T_c$) of the copolymer. Under different test frequencies, the temperatures of the dielectric maxima of the copolymer are almost the same, which is characteristic of normal ferroelectric materials. When a bulky termonomer CFE is incorporated into the polymer chain, the $\varepsilon$-$T$ curve shows remarkable change, as shown in Figure 2-1 (b). The terpolymer with this composition has nearly the same VDF/TrFE ratio, and the large change of dielectric properties is due to the incorporation of CFE in the polymer chain. From the figure, it can be seen that the dielectric maxima of the terpolymer shift to room temperature. The dielectric constant also shows very large frequency dispersion, and the

Figure 2-1: Comparison of the different dielectric behaviors of (a) P(VDF-TrFE) copolymer (65/35) and (b) P(VDF-TrFE-CFE) (63/37/7.5) terpolymer.
temperatures of the dielectric maxima move to a higher temperature with measurement frequencies. All of these features suggest that incorporation of CFE into the P(VDF-TrFE) polymer converts the copolymer from normal ferroelectric into relaxor ferroelectric.[4,5] Because the dielectric peak is now at room temperature, the dielectric constant of terpolymer is greatly improved. The dielectric constant of the terpolymer (~55 at 1 kHz) is much larger than that of the copolymer (~15 at 1 kHz) at room temperature.

Incorporation of CFE into the P(VDF-TrFE) copolymer also has a great effect on the high field dielectric properties. Figure 2-2 shows the comparison between bipolar P-E loops of the P(VDF-TrFE) copolymer and the P(VDF-TrFE-CFE) terpolymer. Addition of CFE to the polymer chain greatly reduces the remnant polarization ($P_r$) and coercive field ($E_c$) of the copolymer, but the maximum polarization of the copolymer is higher than that of the terpolymer. For energy storage and pulse power capacitor applications, the usable energy density of these polymers is shown in the shadowed area in Figure 2-2. From the figure, it is obvious that the energy density of the terpolymer is much higher than that of the copolymer because of the great reduction of the remnant polarization.

![Figure 2-2: Comparison of the bipolar P-E loops between the P(VDF-TrFE) copolymer and P(VDF-TrFE-CFE) terpolymers.](image-url)
2.2.2 Structure change associated with change of dielectric properties from copolymer to terpolymer

For the P(VDF-TrFE) copolymer, due to the steric hindrance effect of TrFE, all-trans conformation will be adopted. All-trans conformation is the most polar phase in the PVDF-based polymer, and the P(VDF-TrFE) copolymers show normal ferroelectric properties. When CFE is copolymerized with P(VDF-TrFE), the bulky CFE breaks the ferroelectric ordering of the ferroelectric phase. At room temperature, the ferroelectric phase can no longer remain stable and the non-polar phase becomes dominant.[6] This is accompanied by the conversion of polymer chains from polar all-trans conformation to non-polar TG conformation. Figure 2-3 shows the FT-IR spectra of PVDF copolymer and terpolymer. In this figure, the bands at about 505, 610, 850 and 1290 cm\(^{-1}\) correspond to vibration modes in T\(_{3G}\), TGTG, T\(_{m>4}\) and T\(_{3G}\), and T\(_{m>4}\) conformations, respectively.[1] As seen from the figure, by incorporation of less 8 mol\% CFE in P(VDF-TrFE), the intensity of the polar conformation T\(_{m>4}\) almost disappears in the terpolymer and that of the non-polar TG conformation increases.

![Figure 2-3: FT-IR Spectra of the P(VDF-TrFE) (65/35) copolymer and P(VDF-TrFE-CFE) (63/37/7.5) terpolymer.](image-url)
This microstructure change is directly related to the difference of dielectric properties between the terpolymer and copolymer. Modeling demonstrates that CFE stabilizes the non-polar phase and reduces the energy barrier between the non-polar phase and polar phase, leading to the higher dielectric constant of the terpolymer, compared with that of the copolymer.[7]

### 2.2.3 Dielectric energy density of the P(VDF-TrFE-CFE) terpolymer and its dependence on compositions

Figure 2-4 compares the bipolar P-E loops of the P(VDF-TrFE-CFE) terpolymers with compositions of 63/37/7.5 and 70/30/8.1. In these terpolymers, the amount of CFE is almost the same and the difference in compositions is the VDF/TrFE ratio. The 70/30/8.1 terpolymer has much higher induced polarization than the 63/37/7.5 terpolymer. The reduction of polarization response with decreasing VDF/TrFE ratio is reasonable because compared with TrFE, VDF has a higher dipole moment. Moreover, the 70/30/8.1 terpolymer shows more characteristics of normal ferroelectric behavior than does the 63/37/7.5, higher remnant polarization and higher coercive field, indicating that more

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Figure 2-4: Bipolar P-E loops of P(VDF-TrFE-CFE) terpolymers with the compositions of 70/30/8.1 and 63/37/7.5.
CFE is needed to transform the P(VDF-TrFE) (70/30) copolymer from normal ferroelectric to relaxor ferroelectric.

Figure 2-5 shows the unipolar P-E loops of the terpolymers with the compositions of 63/37/7.5 and 70/30/8.1. The PVDF terpolymer with the compositions of 70/80/8.1 also shows a higher polarization level than the 63/37/7.5 measured from the unipolar P-E loops.

Because the energy density of the terpolymer is the area encircled by the unipolar P-E curve and Y-axis, the shape of the P-E loops also has a significant effect on the energy density. Unlike many other linear dielectric polymers, the P-E loops of terpolymers are highly nonlinear. When a threshold electric field is reached, the increase
of the polarization response slows down, as seen in Figure 2-5. For the 70/80/8.1 terpolymer, when the electric field is higher than 100 MV/m, the slope of the P-E loop decreases greatly. Compared with the 70/30/8.1 terpolymer, the variation of slope of the 63/37/7.5 terpolymer with electric field is more gradual. As a result, although the 70/80/8.1 terpolymer has a higher polarization response, its energy density is almost the same as the 63/37/7.5 terpolymer, as shown in Figure 2-6. In this figure, the energy density of other terpolymers and the P(VDF-TrFE) (75/25) copolymer is also shown for comparison. The different dielectric nonlinearity of the terpolymer related to the different VDF/TrFE ratios in these terpolymers suggests the importance of formulation design to obtain higher energy density.

![Energy density of P(VDF-TrFE-CFE) terpolymers with various compositions.](image)

Figure 2-6: Energy density of the P(VDF-TrFE-CFE) terpolymers with various compositions.

As also shown in Figure 2-6, PVDF-based terpolymers possess much higher energy density than the P(VDF-TrFE) copolymer, suggesting the significance of defect modification. S. Zhang, et al., studied the conformation change with electric field application using FT-IR.[8] It was found when an electric field was applied to the terpolymer, the chain conformations tended to change from a less polar phase to a more polar phase. After the electric field was removed, the induced polar phase could switch back to the original non-polar state. This is the reason that very small remnant
polarization and higher energy density are observed in the terpolymer, compared with copolymers, which are already in the polar state.

Due to the nonlinear dielectric response under a high electric field $E$, the energy density of terpolymers increases almost linearly with electric fields $E$, unlike most linear dielectric materials, such as BOPP, in which the energy density is a function of $E^2$. To quantify the dielectric nonlinearity of the terpolymer, the effective dielectric constant $\varepsilon_{\text{eff}}(E)$ is introduced:

$$U_e = \frac{1}{2} \varepsilon_{\text{eff}}(E)\varepsilon_0 E^2$$  \hspace{1cm} 2.1

In this equation, $U_e$ is the discharged energy density deduced from the P-E loops, shown in Figure 2-6, and $\varepsilon_{\text{eff}}(E)$ is a function of the applied electric field. The variation of the effective dielectric constant with the electric field is presented in Figure 2-7. For these polymers, though their weak field dielectric is about 50-60, their effective dielectric constant decreases quickly with the increasing electric field. When the electric field is 400 MV/m, their dielectric constant is only about 13. The great difference between the weak field dielectric constant and the effective dielectric constant under high electric field suggests using Eq. 1.5 with the weak field dielectric constant to calculate the energy density of dielectric materials in many cases may lead to wrong results.

Figure 2-7: Change of the effective dielectric constant of the terpolymers.
2.2.4 Dielectric and conduction loss of terpolymers

Besides the dielectric constant and energy density, energy loss is another concern for terpolymers for capacitor applications, especially under a high electric field. The energy loss is mainly converted into heat and the released heat increases the temperature of the polymer, which limits the application frequency range of the polymer film under a high electric field and reduces the breakdown field and reliability.

The energy efficiency during a charging and discharging cycle of terpolymers can be roughly evaluated by calculating and comparing the area encircled by the charging curve and discharging curve, and the area encircled by the charging curve and Y-axis on the unipolar P-E loops in Figure 2-5. As shown in Figure 2-8, the discharge efficiency of energy of the terpolymer can change from about 90% to about 65% with increasing electric fields.

![Figure 2-8: Change of the energy efficiency during the charging-discharging cycle of the terpolymers.](image)

The energy loss can be divided into two main parts. The first is the energy loss due to the conduction. The polymer film is not an ideal dielectric material and leakage current is inevitable. The conductivity contribution to the energy loss can be observed on
the unipolar P-E loops. On the P-E loops, when the applied electric field is returned to zero, the polarization response cannot return to zero. The polarization deviation $\Delta P$ between the starting point and ending point on the unipolar P-E loops was thought to be mainly caused by the conduction loss, but the possibility of some slow relaxation processes, such as interfacial polarization, cannot be totally excluded. For the PVDF-based terpolymer ferroelectric relaxor studied here, because of the very fast switching speed of ferroelectric polarization, no “remnant polarization” should be observed on the unipolar P-E loops if there is no conduction loss.

It was further confirmed by experiments that $\Delta P$ on the unipolar P-E loops was mainly caused by the conduction process. Figure 2-9 shows the unipolar P-E loops of the terpolymer acquired under different frequencies. From the curves, it can be observed that $\Delta P$ becomes larger with decreasing frequencies. If $\Delta P$ were due to a certain type of interfacial dielectric relaxation, $\Delta P$ should become smaller with decreasing frequencies. But, on the other hand, the minor contribution of dielectric relaxation can not be excluded.

Figure 2-9: Unipolar P-E loops of the terpolymer measured at various frequencies.
Assuming that $\Delta P$ is fully caused by the conduction and that the conductivity $\sigma$ of the terpolymer doesn’t change with the electric field $E$ (in reality, the conductivity changes with electric fields), the energy loss due to the conduction can be separated approximately from the loss due to polarization hysteresis and dielectric relaxation. The conductivity $\sigma$ of the terpolymer may be calculated from the unipolar P-E loops through:

$$\Delta P = \frac{2 \int_0^{E_{\text{max}}} \sigma E dE}{E_t}$$

where $E_t$ is the ramp rate of the applied electric field (the applied electric field is the unipolar triangular waveform), $E$ is the applied electric field and $E_{\text{max}}$ is the maximum applied electric field.

$$E = E_t \cdot t \quad (\text{for the charging cycle when the field is increased})$$

$$E = E_{\text{max}} - E_t(t - T/2) \quad (\text{for the discharging cycle when the field is decreased})$$

and $E_{\text{max}} = E_t \cdot T/2$

where $t$ is the time at which the electric field $E$ is applied and $T$ is the period of the unipolar triangular applied electric field.

From Eq. 2.2, the conductivity $\sigma$ can be calculated. Then the contribution of conduction to the polarization $P_c$ under a certain electric field $E_a$ on the P-E loops can be calculated as:

$$P_c = \int_0^{E_a} \sigma E dE / E_t \quad (\text{for the charging cycle when the field is increased})$$

$$P_c = \int_0^{E_{\text{max}}} \sigma E dE / E_t + \int_{E_a}^{E_{\text{max}}} \sigma E dE / E_t \quad (\text{for the discharging cycle when the field is decreased})$$

Based on the above equations, the contribution from conduction to the P-E loops can be subtracted from the curves and the polarization returns to zero after the voltage is removed, as shown in Figure 2-10. After the conduction subtraction, the energy loss still
exists, as shown in the figure. This energy loss should mainly come from the dielectric hysteresis loss.

![Graph showing P-E loops](image)

Figure 2-10: Unipolar P-E loops of the terpolymer before and after conduction subtraction.

### 2.2.5 Discharge characteristics of the PVDF-based terpolymers

In order to investigate the discharging characteristic of the terpolymer, a capacitor discharging circuit was designed, as shown in Figure 2-11. In this circuit, the dielectric films are first charged to a given voltage. After that, by closing a high speed (<120 ns) and high voltage switch, the energy stored in the capacitor films is discharged to a resistor load.
To characterize the discharge behavior, different load resistors were used. Dielectric materials can be modeled as an ideal lossless capacitor in series with a resistor (equivalent series resistor, ESR), which represents the loss in the dielectric materials, as shown in Figure 2-12. It is easy to see that when the external load resistor $R_L$ is much larger than the ESR, most of the stored energy will be delivered to the load and thus the

Figure 2-11: Discharge circuit for energy density and discharge speed characterization.

![Figure 2-11](image)

Figure 2-12: An equivalent circuit of a dielectric sample.
measured energy density in the discharge method will be nearly the same as the stored energy density. On the other hand, if \( R_L \) is small, most of the stored energy will be dissipated at the ESR, and the measured energy density from \( R_L \) will be much less than the stored energy density. Therefore, the efficiency of a dielectric capacitor will depend on the load condition and can be very high if \( R_L \gg ESR \).

Using the circuit as shown in Figure 2-11, the discharge behavior of the terpolymer \( P(VDF-TrFE-CFE) \) 63/37/7.5 mol% to a resistor load is characterized. Presented in Figure 2-13 (a) is the discharged energy density to a 1 MΩ load as a function of time for different initial fields in the terpolymer. The total discharged energy density is comparable to the energy density deduced from the unipolar P-E loops, as shown in Figure 2-6. The small signal capacitance of the film samples used here is about 1 nF measured at 1 kHz. Several terpolymer film samples were characterized. Because of the nonlinear and frequency dependence of the polarization responses, the discharge characteristics of the terpolymer cannot be described simply by a RC constant, where \( R \) is the resistance (\( R=R_L+ESR \)). Assuming a capacitor of which the capacitance does not change with frequency as well as the electric field and the RC time constant \( \tau = R_L C + ESR \times C \), \( ESR \times C \) can be ignored if \( R_L \ll ESR \), the discharged energy density vs. time follows:

\[
U_e(t) = U_D(1 - e^{-\left(\frac{2t}{\tau}\right)})
\]

For the sake of comparison, we use the small field capacitance of 1 nF and a load resistor of 1 MΩ to estimate the time for the energy discharge using Eq. 2.5 (ignore ESR). The discharge time for 70% energy release is 0.6 ms and for 50% energy release is 0.35 ms. Experimentally, the time is 0.66 ms and 0.3 ms, respectively. The difference between the estimated and measured values reflects the nonlinear (the effective dielectric constant becomes small at high field (>100 MV/m)) and frequency dependence of dielectric response (the dielectric constant is smaller at a higher frequency or faster discharge time). Furthermore, ESR at a high frequency (or short discharge time) is small and becomes larger at late discharge times.
Figure 2-13: The discharged energy density as a function of time for the terpolymer 63/37/7.5 into (a) a 1 MΩ load, data from different peak fields is shown in different figures. (b) a 1 kΩ load and a 100 kΩ load under a field ~ 250 MV/m. Different curves in each figure are from different terpolymer samples. The small field capacitance of the film samples is about 1 nF, measured at 1 kHz using a LCR meter.
The discharged energy density to other values of a load resistor ($R_L=100 \, k\Omega$ and 1 $k\Omega$) for the same terpolymer film capacitors is shown in Figure 2-13(b). As expected, reduced $R_L$ shortens the discharge time. However, careful inspection of the experimental data reveals that the reduction of the discharge time is not proportional to the reduction of $R_L$. In Table 2-1, we list the discharge time $\tau$ for 70% and 50% energy release for the three load resistor cases. Especially for the 1 $k\Omega$ load case, the time for 50% energy release is 0.2$\mu$s which is more than 1000 times shorter than that in the 1 M$\Omega$ case. The difference is due to the frequency dependence of the dielectric response and at a high frequency (faster discharging time), the effective dielectric constant of the relaxor terpolymer becomes smaller, causing a reduction of the discharge time. The results here also indicate that at a relatively fast discharge time, the ESR effect is not significant. For AC signal with the angular frequency $\omega$, the ESR of a capacitor can be deduced from the dielectric loss $\tan\delta$: [9]

$$ESR = \frac{\tan\delta}{\omega C} \quad (2.6)$$

Table 2-1: The experimental data on the terpolymer capacitor (~ 1 nF at low field and 1 kHz) discharge time

<table>
<thead>
<tr>
<th></th>
<th>$R_L=1 , M\Omega$</th>
<th>$R_L=100 , k\Omega$</th>
<th>$R_L=1 , k\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{50%}$</td>
<td>0.3 ms</td>
<td>0.03 ms</td>
<td>0.2 $\mu$s</td>
</tr>
<tr>
<td>$T_{70%}$</td>
<td>0.66 ms</td>
<td>0.078 ms</td>
<td>0.76 $\mu$s</td>
</tr>
</tbody>
</table>

For dielectric materials with weak dispersion, the ESR decreases with frequency $f$ (~1/f). For the relaxor ferroelectric terpolymer, the dielectric constant decreases and the loss tangent increases with frequency. The net effect is a slower decrease of $\tan\delta/\omega C$ with frequency (see Figure 2-14, deduced from the data in Figure 2-1(b)).
The total discharged energy density of the terpolymer to a different load resistor $R_L$ is summarized in Figure 2-15. With reduced $R_L$, the discharged energy density is reduced, due to the energy loss in the ESR. For a discharge experiment, an effective ESR may be introduced to account for the energy loss in the capacitor; the equivalent circuit in Figure 2-12 implies that the discharged energy density $U_d$ measured from $R_L$ is related to the total stored energy density $U_0$ in the capacitor by:[9]

\[ U_D = U_0 \frac{R_L}{R_L + ESR} \quad 2.7 \]

Figure 2-14: Change of ESR with frequencies of the terpolymer

Figure 2-15: A summary of discharge energy density with different load resistors
It should be emphasized that an ESR thus introduced will not have a fixed value and will depend on \( R_L \). For the terpolymer here, the effective ESR will decrease as \( R_L \) is reduced. As estimated, based on the data in Figure 2-13 for 1 M\( \Omega \) and 100 k\( \Omega \) loads, Eq. 2.7 yields an effective ESR of 10.1 k\( \Omega \). On the other hand, using the data for 100 k\( \Omega \) and 1 k\( \Omega \) load, Eq. 2.7 yields an effective ESR of 0.26 k\( \Omega \). Although these values are some type of averaged value (for example, the effective ESR for a 1 k\( \Omega \) load will be smaller than 0.26 k\( \Omega \), and the effective ESR for 100 k\( \Omega \) will be in between 0.26 k\( \Omega \) and 10.1 k\( \Omega \)), the results do confirm that the effective ESR for the discharge experiment increases with \( R_L \) and meanwhile also provide an approximate range for the effective ESR for each \( R_L \). By conducting the discharge experiment with more closely spaced \( R_L \) values, the effective ESR for each \( R_L \) can be determined and as a result, the efficiency of the capacitor discharging to a given load \( R_L \) can be determined.

2.2.6 Charge injection and conduction in the terpolymers

As mentioned in the previous section, energy loss due to conduction is one of two main loss mechanisms during the charging and discharging process. For the PVDF-based terpolymer, the conduction mechanisms are still not well understood. Therefore, it is necessary to study the conduction mechanisms in the terpolymer to find out if we can reduce the conduction loss.

Many studies have been conducted in the past on the conduction process in the insulation polymer.[10-13] In general, the conduction process in the polymer can be controlled by an electrode-metal interface or the bulk polymer itself.[12,13] F. Xia, et al., observed the electrode dependence of ferroelectric switching in the P(VDF-TrFE) copolymer thin film.[14] The authors attributed this dependence to the different conductivities of the metal-insulator-metal system, which results from the different work functions of metal electrodes. The electrode-dependent conduction was also observed in other polymers.[12,13]
The electrode dependence of the conduction in PVDF-based terpolymers was observed from the measurement of unipolar P-E loops. Figure 2-16 shows the unipolar P-E loops measured in terpolymer samples with gold, aluminum and silver as electrodes. The figure shows that the $\Delta P$, which are mainly caused by conduction loss, as discussed

![Diagram showing P-E loops for different electrodes](image)

**Figure 2-16:** Unipolar P-E loops of the terpolymer P(VDF-TrFE-CFFE) (64/36/7.2) with different electrodes.
above, are different in the samples with different electrodes. The $\Delta P$ of the samples with the gold electrode is about two times larger than the samples with aluminum and silver electrodes. The conduction loss of samples with aluminum and silver electrodes has nearly the same value. Corresponding to lower conduction loss, the energy density and efficiency of samples with the aluminum electrode calculated from the P-E loops are higher than the samples with the gold electrode, as shown in Table 2-2.

Table 2-2: The released energy density, consumed energy density and efficiency of P(VDF-TrFE-CFE) (64/36/7.2) terpolymers with different metal electrodes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electric Field (MV/m)</th>
<th>Released Energy (J/cm³)</th>
<th>Consumed Energy (J/cm³)</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terpolymer with aluminum electrode</td>
<td>310</td>
<td>6.03</td>
<td>1.67</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>327</td>
<td>6.43</td>
<td>1.87</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>6.81</td>
<td>2.09</td>
<td>0.76</td>
</tr>
<tr>
<td>Terpolymer with gold electrode</td>
<td>310</td>
<td>5.87</td>
<td>2.25</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>327</td>
<td>6.24</td>
<td>2.61</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>6.61</td>
<td>2.94</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>6.97</td>
<td>3.3</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Figure 2-17: Conduction of the P(VDF-TrFE-CFE) terpolymer under various electric fields.
By measuring the I-V curves of the terpolymer with different electrodes directly by Keithley 6517A electrometer, dependence of conduction on electrode materials was further confirmed, as shown in Figure 2-17. In this figure, the current was measured 1 min. after the measurement voltage was applied on the samples. Under the same electric field, the current of the sample with the gold electrode is higher than the sample with the silver electrode. Also, the current of both samples shows saturation at certain electric fields. The current of the sample with the silver electrode saturates at a lower electric field than the one with the gold electrode.

It is unclear which charge carrier accounts for the conduction of the terpolymer. It was proposed by several authors that in the PVDF-based polymers, ionic conduction is the conduction mechanism.[13,15] Under the applied electric field, the ionic carriers drift from one electrode to the opposite electrode.[16] The redistribution of ionic carriers will generate an electric field opposite to the applied field, which will reduce the effective electric field applied on the materials and reduce the apparent electric current. This can lead to the current saturation, as mentioned above. Charge injection from the electrode and trap filling is another possible mechanism. Electrons or holes are carriers for conduction in this case. Under an electric field, the electrons or holes can be injected into the polymer from the negative or positive electrodes. The injected charge will fill the traps with certain energy levels in the polymer. In the semicrystalline polymer, as we all know, there are many traps with different energy levels due to the imperfect structure. The electron or hole conduction process occurs through the trapping and detrapping process. The conduction will be reduced when a certain level of the traps is filled, which can also lead to the current saturation.

The thermally stimulated current (TSC) was further measured to identify which mechanism governs the conduction process. Figure 2-18 shows the TSC curves of terpolymer samples with gold. The samples tested were poled at room temperature for 5 min. under an electric field of 25 MV/m. As shown in the figure, a large amount of homocharges were built up during the poling process. When the poled sample is heated, a large thermally stimulated current peak in the direction of poling electric was observed. Because the drift of ionic carriers can only generate hetero-charges, the high thermally
stimulated current should be mainly caused by the injected charges from the electrodes, which are trapped in the polymer near the polymer-metal interface and form homo-space charge. But it is also possible that a small amount of heterocharge (resulting from ionic carriers) coexists with the homocharge, and that during TSC measurement, the large homocharge current screens the heterocharge current. Based on this result, it is reasonable to conclude that the conduction process in the terpolymer is mainly due to the trapping and detrapping process of electron or hole, and that the injected charges provide a large carrier pool for the conduction process. Ionic conduction may exist, but not the main conduction process.

\[ J \propto \exp(-C\Phi^o_B) \]

In this equation, \( \Phi_B \) is the barrier height of the metal-polymer interface determined by the work function of metal and polymer; \( C \) is a parameter independent of \( \Phi_B \). The work functions of aluminum and silver are 4.26 and 4.28 eV, respectively, in contrast to the work function of gold, 5.31 eV. Because the working function of aluminum is close
to that of silver, it is reasonable that samples with silver and samples with aluminum electrodes have similar conduction loss (as observed from the P-E loop).

Besides the work function, it was also thought that the interfacial layer between the polymer and metal was another factor that affects conduction. For the aluminum electrode, during the preparation, oxidation may happen and an insulation layer could be formed between the polymer and metal.[19] The injection of charge may be blocked by the interfacial layer.

From the TSC curve, the trap concentration can be estimated. The total trapped charge, which is calculated by integration of current curve, is about $4.5 \times 10^{-7}$ C in a sample 6 mm in diameter and around 15µm in thickness. It corresponds to a trap concentration of more than $6.6 \times 10^{15}$/cm$^3$, assuming that the charges are uniformly distributed. In reality, the trap density of the polymer should be higher than this value because only part of the traps were filled during the poling process and also because the trapped charges are not uniformly distributed throughout the bulk polymer.

### 2.2.7 Electrical breakdown of the terpolymers

For polymers used in high voltage dielectric applications, the electrical breakdown field is a very important parameter. As we already know, the energy density of dielectric materials is directly related to the breakdown field. Also under the same operation electric field for these dielectric materials, higher breakdown field means higher reliability. Various electrical breakdown mechanisms have been proposed for solid state dielectrics, including thermal breakdown, electromechanical breakdown and electronic breakdown.[20] Here, the breakdown field of the terpolymer and some factors that affect the breakdown field of the terpolymer will be presented.

The breakdown field of the terpolymer film with the composition of P(VDF-TrFE-CFE) 63/37/7.5 was tested. The film was prepared by solution cast and the thickness is 9-11 µm. Gold electrodes with the dimension of 2.5 mm in diameter were sputtered on both sides of the film. The samples were put between two metal electrodes.
with round surfaces. The voltage ramp rate is 500 V/m. Ten samples were tested and the breakdown field is summarized in Table 2-3. As shown in the table, the maximum breakdown field of the terpolymer can be higher than 400 MV/m intrinsically, but due to pinholes or other defects that may exist during the film processing, the breakdown fields spread in a wide range, from about 150 MV/m to about 420 MV/m.

In order to analyze the breakdown field, the Weibull analysis is often used:

\[
F(x) = 1 - e^{-\left(\frac{x}{\alpha}\right)^\beta}
\]

In this equation, \(F(x)\) is the cumulative failure of the tested samples; \(\alpha\) is the characteristic breakdown field, and when breakdown field \(x=\alpha\), 63.2% samples fail; and \(\beta\) is a parameter that indicates the distribution of breakdown field. The data in Table 2-3 were analyzed by the equation and the result is shown in Figure 2-19. The characteristic breakdown field \(\alpha\) is 280 MV/m and \(\beta\) is 2.46.

Table 2-3: Breakdown test result of the terpolymer.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breakdown field (MV/m)</td>
<td>144</td>
<td>173</td>
<td>177</td>
<td>187</td>
<td>225</td>
<td>232</td>
<td>263</td>
<td>273</td>
<td>416</td>
<td>420</td>
</tr>
</tbody>
</table>

The existence of defects in the terpolymer films was confirmed by the SEM images of polymer surface, shown in Figure 2-20. The crystalline and amorphous phases are easily discernable from the pictures. The defects, in the form of cracks, are mainly found in the amorphous phase or amorphous-crystalline phase interface. The width of the cracks is about tens of nanometers, and crack length ranges from tens to hundreds of nanometers. The relatively large spread of breakdown data is probably due to the non-homogeneous distribution of the cracks. These cracks may be caused by the different shrinkage of crystalline (anisotropic) and amorphous (isotropic) phases during the solvent evaporation.
Figure 2-19: Weibull analysis of the breakdown field of the P(VDF-TrFE-CFE) terpolymer (63/37/7.5) with gold electrode ($\alpha$ is 280 MV/m and $\beta$ is 2.46).

Figure 2-20: Surface morphology of the P(VDF-TrFE-CFE) terpolymer.
Consistent with electrode material dependence of conduction, the breakdown field of the terpolymer has a relatively strong correlation with the metal electrode. Figure 2-21 shows the breakdown field of the terpolymer with sputtered silver electrode. The polymer film for this breakdown test was prepared at the same time as the samples with the gold electrode. The electrode size and voltage ramp rate were also the same as the previous test. The characteristic breakdown field $\alpha$ and $\beta$ are 248 MV/m and 2.68, respectively. The breakdown field of samples with the silver electrode is slightly lower than the samples with the gold electrode. The result suggests that the electrode-polymer interface plays an important role in the breakdown process. As discussed above, the differences between the gold and silver electrodes are different work functions and possible different blocking effects, which lead to different charge injection and conduction. The electric field resulting from charge injection may change the electric field distribution in the polymer. The different field distributions in the samples with the gold and silver electrodes may be the dominant factor that affects the breakdown field of the terpolymer. It is reasonable that $\beta$ parameters are almost the same for the both cases because the defect distribution is almost the same if the samples are prepared under the same conditions.

Figure 2-21: Weibull analysis of the breakdown fields of the terpolymer with silver electrode ($\alpha$ and $\beta$ are 248 MV/m and 2.68, respectively).
The importance of the polymer-metal interface for the electrical breakdown of the terpolymer is further confirmed by testing the breakdown field of the terpolymer film coated with a very thin layer of acrylate coating on one surface of the terpolymer.[21] The thin layer of acrylate polymer was coated by electron-initiated polymerization after the deposition of monomers on the terpolymer surface by thermal evaporation. The thickness of the acrylate polymer is about 0.1-0.2 µm. The dielectric constant of the acrylate coating is about 3.

Figure 2-22 shows the Weibull analysis of the breakdown fields of the coated terpolymer. The procedures for the breakdown test were the same as for the uncoated samples. Gold was sputtered as electrode. The breakdown fields exhibit great difference between the samples with the coating layer contacting the anode and these with the coating layer contacting the cathode during the breakdown test. The breakdown field is 274 MV/m when the coating layer faces the anode. In contrast, the breakdown field is 211 MV/m when the coating layer faces the cathode. Although the mechanisms for this large polarity of the breakdown field are not clear, this result clearly suggests that the metal-polymer interface and the charge injection from the metal to the polymer play important roles for the breakdown process of the terpolymer. It should be pointed out that the terpolymer films for coating and for the breakdown test (the result is shown in Figure 2-19 and Figure 2-21) was from different batches. Therefore, the breakdown may not be comparable for uncoated (Figure 2-19 and Figure 2-21) and coated films (Figure 2-22). Also, the film coating was performed by a company (Sigma Technology). Due to the possible damage of the films during the coating process, the breakdown field of the coated samples is somewhat lower than uncoated terpolymer.
In this chapter, various characterizations were carried out on P(VDF-TrFE-CFE) terpolymers to evaluate their performance as dielectric materials of high energy density for capacitor applications. Compared with the P(VDF-TrFE) copolymer, due to the defect modification by bulky CFE, the nonpolar phase was stabilized in the terpolymer and the energy barrier between the nonpolar phase and the polar phase was reduced. The energy density of the terpolymer was much larger than that of the copolymer due to the reversible change between these two phases.

Two different methods (i.e., the Sawyer-Tower circuit method to measure the polarization response and the direct discharge method to measure the discharged energy to a resistor load) were employed to characterize the discharged energy density of the ferroelectric relaxor P(VDF-TrFE-CFE) terpolymer. The unipolar polarization loops yield a discharged energy density $\sim 10 \text{ J/cm}^3$, obtained under an electric field of more than $350 \text{ MV/m}$. The nonlinear dielectric response under the high field of the terpolymer is manifested by the nearly linear dependence of the discharged energy density with the applied field, which is distinctively different from the low dielectric constant linear dielectric polymers whose energy density rises with the square of the applied field.

Figure 2-22: Breakdown test results for (a) the samples with coating layer facing cathode ($\alpha=211 \text{ MV/m}$ and $\beta=5.7$) and (b) the samples with coating layer facing cathode ($\alpha=274 \text{ MV/m}$ and $\beta=4.5$).

2.3 Summary

In this chapter, various characterizations were carried out on P(VDF-TrFE-CFE) terpolymers to evaluate their performance as dielectric materials of high energy density for capacitor applications. Compared with the P(VDF-TrFE) copolymer, due to the defect modification by bulky CFE, the nonpolar phase was stabilized in the terpolymer and the energy barrier between the nonpolar phase and the polar phase was reduced. The energy density of the terpolymer was much larger than that of the copolymer due to the reversible change between these two phases.

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The strong frequency dispersion and nonlinear polarization response (polarization saturation) of the relaxor terpolymer result in a low effective capacitance at the beginning of the discharge cycle of the terpolymer and the effective capacitance increases with time during the discharge cycle. In addition, the discharged energy density of the terpolymer to a resistor load $R_L$ increases with $R_L$ due to the frequency dispersion and nonlinear effect in the terpolymer. A large $R_L$ will lead to a high discharge efficiency. For a terpolymer capacitor of 1 nF (measured at a low field at 1 kHz) discharging to a 1 MΩ load, most of the stored energy can be discharged within 1 ms, and to a 0.1 MΩ load, this time is reduced to 0.1 ms.

The discharged energy densities determined by each of the two methods are consistent with each other. For example, the discharged energy densities to 1 MΩ and 0.1 MΩ load resistors are more or less the same as that deduced from the unipolar hysteresis loops.

The interface between the metal electrode and the polymer was found to play a very important role in the high field conduction and dielectric breakdown of terpolymers. High field conduction, as well as dielectric hysteresis loss, is the mechanism for energy loss during the energy charging and discharging process. The conduction of the terpolymer is mainly controlled by the charge injection through the polymer-electrode interface. By using aluminum and silver as electrodes, the conduction of the terpolymer can be decreased, which can further reduce the energy loss. Injected holes or electrons, rather than ions, are the charge carriers for the conduction in the bulk polymer. The injected charge may also form space charge and modify the local electric field in the terpolymer, which is the main reason for the dependence of the breakdown field with electrode materials. The great effect of the polymer-metal interface on the breakdown field was further confirmed by the large polarity of the breakdown field of acrylate-coated terpolymers.
References


Chapter 3

The PVDF-based Copolymers of High Energy Density

3.1 Introduction

In Chapter 2, the P(VDF-TrFE-CFE) terpolymers have been demonstrated as a group of dielectric polymers with high energy density (energy density $U_e > 9$ J/cm$^3$). The high energy density comes from their high dielectric constant $\sim 55$ at room temperature (at 1 kHz) and relatively high breakdown field (as high as 400 MV/m). However, the high dielectric constant of the terpolymers also leads to the highly non-linear dielectric response under the high electric field and fast saturation of polarization response. As already shown in the proceeding chapter, because of the non-linear dielectric response, the energy density of the terpolymer is almost proportional to the applied electric field rather than the square of the electric field.

For the PVDF-based polymers, the maximum induced polarization level is almost the same (for $\beta$ phase PVDF homopolymer, the maximum polarization is around 0.13 C/m$^2$). The induced polarization will be saturated (reach maximum polarization) under a high applied electric field. Accompanying the polarization saturation, significant change of the non-linear dielectric response can be observed. If the polarization saturation is far below the breakdown field, the dielectric material may not reach the full potential in achieving high electric energy density.

A larger dielectric constant implies faster polarization saturation. Figure 3-1 schematically shows the relationship among dielectric constant, breakdown field and induced polarization for dielectric materials with a given saturation polarization $P_{sat}$ or $D_{sat}$. In this figure, a piece-wise polarization response is used to approximate the polarization response of the dielectric materials. As seen from the figure, a very high dielectric constant at low field can lead to an “early” saturation of the polarization (curve
I). That is, the material reaches the polarization saturation at a field greatly below the breakdown field. In this sense, a very high dielectric constant at low field is not a desirable feature for a dielectric material to reach high electric energy density. Instead, a dielectric constant (smaller dielectric constant) which maximizes the electric energy density as schematically shown in figure (curve II) is desirable. Therefore, based on this consideration, in this chapter, defect modified polyvinylidene fluoride (PVDF) copolymers, P(VDF-CTFE) (CTFE: chlorotrifluoroethylene) and P(VDF-HFP) (HFP: hexafluoropropylene), which have a dielectric constant around 12 (at 1 kHz), much lower than the terpolymer, but still much larger than other linear dielectric materials for capacitor applications, will be studied as candidate materials of high energy density.

In recent years, P(VDF-CTFE) and P(VDF-HFP) copolymers have been investigated as polymer materials with good electromechanical properties.[1-7] In this chapter, we will show that the copolymers also possess very high dielectric energy density for capacitor applications (higher than 24 J/cm³).

Figure 3-1: Schematic illustrating the relationship among the dielectric constant, polarization saturation, and breakdown field of the dielectric materials.
3.2 Experimental

P(VDF-CTFE) (the weight percentage of CTFE is 10, 15 and 20 wt%) and P(VDF-HFP) (the weight percentage is 10 and 12 wt%) copolymers were purchased from Solvay and 3M. Because the copolymer films prepared by the solution casting method always show low breakdown field, the polymer films for the electrical test were prepared by compression molding at 230°C for 5-10 min. The film prepared by compression molding was found to exhibit better quality and higher breakdown field than that prepared by solution cast method. The films were quenched to room temperature after compression molding. For some measurements, the film was stretched uniaxially to about four times its original length by the zone drawing method in the temperature range between 110°C and 140°C.[8,9]

The procedures for electrode deposition, weak-field and high-field dielectric measurement, and breakdown test are the same as in the proceeding chapter.

The glass-transition temperature, melting point, crystallization temperature and crystallinity of the copolymers were studied by the differential scanning calorimetry (DSC, TA Q100). The mechanical properties were measured by a dynamic mechanical analyzer (DMA, TA2980). The microstructure of the copolymers was characterized by X-ray diffraction (Scintag CuKα diffractometer) and Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 510).

3.3 Experimental results and discussions

3.3.1 Dielectric property and energy density of the P(VDF-CTFE) (15 wt% CTFE) and P(VDF-HFP) (10 wt% HFP) copolymers

As already demonstrated in the proceeding chapter, by employing the defect modifications, the P(VDF-TrFE) copolymers at compositions below VDF/TrFE 70/30 mol% can be converted into a ferroelectric relaxor in which the remnant polarization is near zero and a large polarization change can be obtained. The relaxor ferroelectric
behavior was attained by the reduction of the energy barrier of molecular conformation change between the non-polar and polar conformations.[10-12] However, this defect modification also results in a larger dielectric constant and lower dipole density than PVDF homopolymer and P(VDF-TrFE) copolymers.

For the PVDF homopolymer, the energy difference between the TGTG’ and all-trans conformations is very small, which may be utilized to generate a large polarization change without the penalty of a high dielectric constant at low electric fields. Recent simulation results have shown that, in fact, for a single molecular chain, TGTG’ conformation has a lower energy compared with the all-trans conformation while in the crystalline phase; the inter-chain coupling lowers the energy of the all-trans conformation with respect to the TGTG’ conformation. Therefore, by defect modifications which expand the inter-chain lattice spacing, one may lower the energy of the TGTG’ conformation and achieve a reversible conformation change between the $\alpha$-phase and $\beta$-phase which can lead to a large polarization change without the penalty of a very high dielectric constant at low field and the early polarization saturation.[13,14] Based on these considerations, random copolymers of P(VDF-CTFE) and P(VDF-HFP), in which the bulkier size of CTFE or HFP compared with VDF may expand the inter-chain space and distort the crystalline ordering, were studied.

Figure 3-2(a) shows the temperature dependence of the dielectric constant and dielectric loss of P(VDF-CTFE) (15 wt% CTFE) at various frequencies. The dielectric constant of the copolymer at room temperature is about 12 (1 kHz). Based on the discussion above, for the PVDF-based polymer with such a dielectric constant, the polarization will saturate under a higher electric field and higher energy density may be obtained. The dielectric constant of P(VDF-HFP) (10 wt% HFP) at 1 kHz is also around 12, which is another potential dielectric material with high energy density, as shown in Figure 3-2(b). For these two copolymers, the variation of the dielectric constant with temperature (in the temperature range from room temperature to more than 100°C) is small, which is attractive for the dielectric applications that require a stable dielectric response over a wide temperature range. In the figure, similar to the PVDF homopolymer, two relaxation processes can be observed, which will be discussed later.
To obtain the energy density of the copolymers, the unipolar P-E loops of unstretched and stretched P(VDF-CTFE) (15 wt% CTFE) and P(VDF-HFP) (10 wt% HFP) copolymer films were measured and are shown in Figure 3-3. For unstretched copolymers, as expected, because of their lower dielectric constant in comparison with the terpolymer, their P-E loops exhibit much less non-linearity even under an electric field higher than 400 MV/m, which is shown in Figure 3-3(a) and (c). The discharged energy density of unstretched samples was calculated from the P-E loops and is shown in Figure 3-4(a) and (b). Due to the considerably less nonlinearity, the energy density of
copolymers increases almost quadratically with electric field, in contrast to the linear relationship between electric field and energy density for the terpolymers. Under an electric field of about 400 MV/m, the energy density of copolymers is nearly the same as that of PVDF-based terpolymers.

After stretching, the breakdown field of copolymer film was greatly improved. As shown in Figure 3-3(b) and (d), the maximum applied fields on the copolymer film for P-E measurement were increased from about 450 MV/m to more than 500 MV/m. The improvement of the breakdown field is due to the orientation effect of the polymer chain and the improvement of the mechanical properties of the film by stretching.[15] The

Figure 3-3: Unipolar P-E loops of (a) unstretched (b) stretched P(VDF-CTFE) (15 wt% CTFE) copolymer (c) unstretched and (d) stretched P(VDF-HFP) (10 wt% HFP) copolymer.
second effect of stretching is reduction of loss although the mechanisms for the loss reduction are not clear, as seen from the figure. The third effect of the stretching is the improvement of polarization response. Under the same field, the polarization level of stretched film is higher than that of unstretched film, presumably due to the orientation effect of the polymer chain.

The discharged energy density of stretched copolymer film was calculated from the P-E loops and is also shown in the Figure 3-4(a) and (b). For the stretched P(VDF-CTFE) and P(VDF-HFP) copolymers, improvement of the breakdown field and polarization response leads to very high energy density. For the P(VDF-CTFE) copolymer, a maximum energy density of 17.5 J/cm³ under an electric field of 575 MV/m, and for the P(VDF-HFP) copolymer, a maximum energy density of about 12 J/cm³ under an electric field of 520 MV/m, can be obtained. As expected, the energy density obtained in these copolymers is much higher than in the terpolymer.

![Graph](image)

Figure 3-4: Discharged energy density calculated from the P-E loops of (a) stretched and unstretched P(VDF-CTFE) (15 wt% CTFE) copolymer and (b) stretched and unstretched P(VDF-HFP) (10 wt% HFP) copolymer.

Besides compression molding method, the copolymer films were also prepared by the extrusion-blown method in relatively larger scale than the compression molding method.[16] The extrusion-blown method was found to greatly improve the quality of the film and the breakdown field, probably due to the smaller amount of contamination from the environment during the relative large scale processing. Figure 3-5 shows the Weibull
analysis of the breakdown field of the P(VDF-CTFE) copolymer film prepared by the blown method. The thickness of the samples for the breakdown test is around 15-20 µm and the electrode (gold) size is 6 mm in diameter. The characteristic breakdown field is 639 MV/m with a large shape parameter \( \beta \) of about 10. The maximum breakdown field of the copolymer is 686 MV/m. The data point in the inset of Figure 3-5 shows dependence of energy density on the applied electric field from the measurement results (part of Figure 3-4(a)) and the curve on the inset is the quadratic fitting of these data points. The energy density corresponding to a breakdown field of 686 MV/m is higher than 24 J/cm\(^3\), which can be deduced from the fitting curve.

![Figure 3-5: Weibull analysis of the breakdown field of P(VDF-CTFE) (15 wt% CTFE) copolymer film prepared by the extrusion-blown method. The inset in the figure shows the fitting curve of the energy density of the copolymer under various electric fields.](image)

The discharge characteristics of P(VDF-CTFE) copolymer films were further investigated by the discharge circuit described in Chapter 2, in which the discharged energy was measured from a load resistor \( R_L \) in series with the polymer capacitor. The change of discharge energy to load resistors with time is shown in Figure 3-6. For P(VDF-CTFE) capacitor films of 0.16 nF (measured at low field and 1 kHz) discharging to a 1 kΩ load, the energy discharging time is much below 1µs. As the load resistor value changes from 1 kΩ to 100 kΩ, the discharging time increases by a factor of 100. This
indicates that the discharge time is mainly controlled by the capacitance of the copolymer film and external load resistor $R_L$. The P(VDF-CTFE) copolymer capacitor can have a very fast discharge time ($<1 \mu s$). In fact, the fitting to the voltage change $V(t)$ across the load resistor yields a time constant nearly the same as that deduced from $R_L C$.

3.3.2 Composition-structure-property relationship of P(VDF-CTFE) copolymers

3.3.2.1 Weak field dielectric properties

Figure 3-6: Discharge energy density as a function of time measured from the direct discharge of the P(VDF-CTFE) polymer films to a resistor load $R_L$. (a) $R_L=100 \text{k}\Omega$ and (b) $R_L=1 \text{k}\Omega$. The energy density for $R_L=100 \text{k}\Omega$ is 3.47 J/cm$^3$ and for $R_L=1 \text{k}\Omega$ is 3.25 J/cm$^3$. The electric field is 253.5 MV/m.

Figure 3-7 shows the temperature dependence of weak field dielectric properties of P(VDF-CTFE) copolymers with different weight percentages of CTFE (10, 15 and 20 wt%). The dielectric constant of these copolymers at room temperature is around 11-13. Similar to the 15 wt% CTFE copolymer, the dielectric constant of the other two compositions exhibits small variation in the whole temperature range of the measurement.
Figure 3-7: Temperature dependence of dielectric properties of P(VDF-CTFE) (a) 10 wt% CTFE (b) 15 wt% CTFE and (c) 20 wt% CTFE copolymers.
To compare the dielectric properties of these copolymers more clearly, the dielectric constant and loss of these copolymers at 1 kHz are summarized in Figure 3-8(a) and (b), respectively. In Figure 3-8(a), because the film thickness of samples prepared by compression molding was not very uniform and the sample size was relatively large, the measurement error of the dielectric constant was a little large. In this figure, the dielectric constant of the 10 wt% CTFE copolymer at -30°C was taken as a reference. For the purpose of comparison, the curves of the dielectric constant vs. the temperature (ε−T) of other compositions were divided by a factor to adjust the dielectric constant at this temperature so that it is the same for all the compositions.

Analogous to the PVDF homopolymer, two loss peaks can be observed in the temperature range from -30°C to 150°C, as shown in Figure 3-8(b). The first peak around -30°C at 1 kHz was assigned to the glass transition, but considering that the dielectric constant of PVDF and the copolymers reaches the dielectric maxima around this temperature, as shown in Figure 3-8(a), and the high dielectric response of PVDF-based polymers results mainly from the crystalline phase, this peak may also be related to the crystalline phase, probably due to the relaxation process in the crystalline-amorphous interphase.[17] The slight shift of this loss peak from -25°C for the homopolymer to -21°C for the copolymer with the 20 wt% CTFE can be observed in Figure 3-8(b). If we assume only glass transition accounts for this peak, the glass transition temperature of the 20 wt% copolymer can be calculated as:[18]

\[ T_g = \frac{1}{W_1/T_{g1} + W_2/T_{g2}} \]

Where \( T_{g1} \) and \( T_{g2} \) are glass transition temperatures of pure PVDF and PCTFE; \( W_1 \) and \( W_2 \) are respective weight fractions of two components in the copolymer. The glass transition temperature of PCTFE is 50°C (323 K).[19] The calculated glass transition of the 20 wt% CTFE copolymer is -13°C (260 K), much higher than the experimental result. Therefore, the experimental result supports the above conclusion that other relaxation mechanisms, such as the relaxation process in the crystalline-amorphous interphase, contribute to the dielectric loss peak at around -30°C.
A dielectric maximum around 110°C at 1 kHz on $\varepsilon$–$T$ curve of the PVDF homopolymer can be observed, as shown in Figure 3-8(a). Corresponding to this dielectric maximum, a loss peak around 80°C on the loss curve of the PVDF homopolymer, as shown in Figure 3-8(b), can also be observed. This dielectric maximum

Figure 3-8: Comparison of (a) dielectric constant and (b) dielectric loss at 1 kHz of the PVDF homopolymer and the P(VDF-CTFE) copolymers with various compositions.
at 110°C for the homopolymer was considered by several authors to be associated with the motions of loops attached to the folded structure of the crystalline phase or the defects in the crystalline phase. Our experimental results support the explanation that this dielectric peak may be associated with the defects in the crystalline phase.[17] As shown in Figure 3-8(a), this dielectric maximum is gradually suppressed with CTFE content. With an increasing amount of CTFE, the magnitude of this dielectric maximum becomes weaker and peak position shifts to a lower temperature. This result suggests that incorporation of CTFE into the polymer chain modifies the crystalline phase of PVDF and reduces the magnitude of the dielectric maximum. Reduction of the magnitude of the dielectric peak may also be related to the decrease of crystallinity with CTFE content, as will be shown later by DSC data.

3.3.2.2 Thermal analysis

Figure 3-9(a) shows the DSC results around the melting temperature of the PVDF homopolymer and its copolymers with CTFE. All the DSC traces were from the second heating cycle of measurement after the samples were heated to 220°C. For the homopolymer, a peak at about 169°C is observed. For P(VDF-CTFE) copolymers, two melting peaks, one at about 167°C and the other at about 160°C, can be observed. The first peak of these copolymers does not change with CTFE, but the second peak is reduced from about 161°C for the 10 wt% CTFE copolymer to 158°C for the 20 wt% CTFE copolymer. It is very interesting that the overall melting temperature of the copolymers does not change significantly even when 20 wt% (12 mol%) of CTFE is copolymerized with VDF. From a theoretical standpoint, incorporation of the bulky monomer in the VDF should reduce the melting temperature.[18] These copolymers, as described in the patent from Solvay, because of the quite different reactivity of VDF and CTFE monomers during polymerization, possess highly heterogeneous composition distribution.[20] The reaction rate of CTFE is much faster than that of VDF, which leads to very large amount of CTFE in the amorphous phase. Experimental results showed that P(VDF-CTFE) copolymer with the 20 mol% (about 33 wt%) CTFE would be an
Figure 3-9: (a) DSC curves around melting temperature of the PVDF homopolymer and P(VDF-CTFE) copolymers with various compositions (b) change of heat of fusion with weight percentage of CTFE and (c) DSC curves around crystallization temperature of the PVDF homopolymer and P(VDF-CTFE) copolymers.
amorphous polymer.[21] The crystalline phase, as mentioned in the patent, is quasi-PVDF phase. The high heterogeneity could explain the slight change of the melting temperature of P(VDF-CTFE) copolymers, compared with that of the PVDF homopolymer.

Based on the description of the patent, the two melting temperatures of the P(VDF-CTFE) copolymers can be explained as two different types of crystalline phases, one almost pure PVDF phase whose peak position does not change with composition, and one CTFE modified PVDF phase whose peak position shifts to a lower temperature with CTFE incorporation.

Change of heat of fusion with compositions of the copolymers is summarized and shown in Figure 3-9(b). The heat of melting decreases exponentially with CTFE content, from 57 J/g for the PVDF homopolymer to 16 J/g for the 20 wt% CTFE copolymer. This result is consistent with the previous report that CTFE could greatly reduce the crystallinity due to the structural irregularity.[21]

Incorporation of CTFE into PVDF also significantly reduces the crystallization temperature, as shown in Figure 3-9(c). The crystallization temperature of the PVDF homopolymer is about 140°C at a 10°C/min cooling rate and that of the copolymer with 20 wt% CTFE is reduced to about 128°C.

Figure 3-10 shows the temperature dependence of the storage modulus of P(VDF-CTFE) copolymers measured by DMA. The storage modulus of the copolymers decreases quickly with CTFE content. At room temperature, the modulus of the copolymer with 20 wt% CTFE is about 200 MPa, in contrast to around 2 GPa for the homopolymer. For film capacitor application, higher modulus will make film processing much easier.
3.3.2.3 FT-IR spectra of the P(VDF-CTFE) copolymers

The chain conformations of the P(VDF-CTFE) copolymers were studied by FT-IR and the spectra of stretched (to about 4 times the original length) copolymers with 10, 15 and 20 wt% CTFE are shown in Figure 3-11. The absorbance peaks at about 550cm\(^{-1}\), 614cm\(^{-1}\) and 1280cm\(^{-1}\) are corresponding to the CF\(_2\) stretching vibration of all-trans conformation (\(T_{m+4}\)), bending mode of CF\(_2\) in the T\(_3G\) conformation and TG conformation in the PVDF-based polymer.[22,23] Their relative absorbance intensity represents the relative ratio of these conformations in the polymers. The figure shows that a significant amount of all-trans conformation still exists in these copolymers, but its intensity decreases with increasing CTFE, which suggests the decreasing amount of the all-trans conformation with CTFE content in the copolymers. The overall intensity of T\(_3G\) and TG conformations increases concomitantly. This experimental result suggests that incorporation of the bulky comonomer CTFE in PVDF tends to favor the nonpolar conformation.
XRD data of the P(VDF-CTFE) copolymers

The XRD patterns of unstretched P(VDF-CTFE) copolymers are shown in Figure 3-12. Consistent with DSC results, the diffraction intensity ratio of crystalline phase to amorphous phase decreases with the increasing amount of CTFE due to the reduction of crystallinity. For all CTFE copolymers, the intensity ratio between the crystal peak and the amorphous halo is low because of their low crystallinity. For the 10 wt% CTFE copolymer with the highest crystallinity, the heat of fusion is only 27J/g, corresponding to about 25% crystallinity, if the heat of fusion of 100% crystalline PVDF was taken as 104.7 J/g.[24] Although a significant amount of all-trans conformation was observed from FTIR in the copolymers, the XRD patterns can be indexed as α phase, as shown in Figure 3-12(a), which is consistent with other reported results. It is interesting to note that, with an increasing amount of CTFE, the diffraction peak shifts to a higher angle. It was thought to be related to the increase of β/α phase ratio by some authors.[21]
However, from the FT-IR result, the amount of all-trans conformation in the copolymers was reduced by incorporation of CTFE into the polymer chain. The reason for the shift of the peak is not clear, probably not due to the crystal structure change (quenching probably is one reason).

For the stretched films, the XRD result shows that they still retain the α-phase-like structure, as shown in Figure 3-12(b). The intensity of the diffraction peak of (100), (020) and (110) was increased due to the orientation effect and the increase of

Figure 3-12: XRD patterns of (a) unstretched (b) stretched P(VDF-CTFE) copolymers; in the two figures, the XRD pattern with the lowest intensity corresponds to the 20 wt% CTFE copolymer and the highest intensity corresponds to the 10 wt% CTFE (c) change of ferroelectric domain size with composition and (d) XRD patterns of stretched and unstretched PVDF homopolymer.
crystallinity by stretching. Except the 10 wt% copolymer, the peaks at around 2θ=26° disappear after stretching also because of the orientation effect of the film. The peak position of (110) diffraction shifts slightly to a lower angle, which is different from the upward shift as observed in the unstretched films, which can be explained as the expansion of the crystal lattice by the bulky comonomer.

The ferroelectric domain size D_{hkl} can be estimated from the full width at half maximum (FWHM) of the diffraction peaks. By employing the Scherer equation, the domain size can be calculated as:[25]

\[ D_{hkl} = \frac{0.9 \lambda}{B \cos \theta} \]

where \( \lambda \) is the wavelength of X-ray, B is the FWHM of the peak (hkl), and \( \theta \) is the peak position. By fitting the XRD patterns using JADE software, the diffraction peak can be fitted and the FWHM can be calculated. The change of the calculated domain size \( D_{110} \) of stretched P(VDF-CTFE) (15 wt% CTFE) copolymers is shown in Figure 3-12(c). The domain size \( D_{(110)} \) decreases from about 13nm for the 10 wt% CTFE copolymer to about 7nm for the 20 wt% CTFE copolymer. As expected, quite similar to the case of the P(VDF-TrFE-CFE) terpolymer, the comonomer CTFE acts as a defect, breaks up the polarization ordering and reduces the domain size of PVDF.

As a comparison, the XRD patterns of unstretched and stretched PVDF homopolymer are shown in Figure 3-12(d). The crystal structure of the PVDF film prepared by compression molding is close to α phase. After stretching, PVDF was transformed into a structure close to β phase. By comparing the results in Figure 3-12(a), (b) and (d), it can be concluded that incorporation of the bulky CTFE comonomer into PVDF can stabilize the α phase to some extent.

### 3.3.2.5 Effect of CTFE on the ferroelectric properties of the PVDF-based copolymers

The polarization hysteresis under the electric field is one of two features for ferroelectric materials. For ferroelectric materials for piezoelectric applications, large
hysteresis is desirable, but for energy storage applications, large hysteresis will reduce the released energy stored in the materials. Therefore, ferroelectric materials with small hysteresis and small remnant polarization are desirable for energy storage and discharge applications. The effect of incorporation of CTFE into the PVDF polymer on the ferroelectric properties is shown in Figure 3-13, in which the bipolar P-E loops of \( \alpha \)-phase PVDF and the copolymer with 15 wt% CTFE are compared. As shown in the figure, the remnant polarization of the copolymer is greatly reduced compared with that of the PVDF homopolymer. There are two reasons for the reduction of remnant polarization: the first is the reduction of crystallinity by copolymerization of CTFE with VDF, which could also reduce the maximum induced polarization, and the second is the destruction of polarization ordering in the copolymer, similar to that of the terpolymer, which makes the ferroelectric domain less stable.[26]

![Figure 3-13: Bipolar P-E loops of \( \alpha \) phase PVDF and the P(VDF-CTFE) copolymer with 15 wt% CTFE.](image-url)
3.3.2.6 Unipolar P-E loops and Energy density of the P(VDF-CTFE) copolymers

The unipolar P-E loops under 350 MV/m of stretched P(VDF-CTFE) copolymers with 10, 15 and 20 wt% CTFE were compared and shown in Figure 3-14. As seen from the figure, under the same electric field, the induced polarization level of the three compositions is almost the same. This means that the released energy density calculated from the loops is also almost the same.

For the ferroelectric polymers, the dielectric response comes mainly from the crystalline phase. As seen from DSC data, the crystallinity of the 10 wt% CTFE copolymer is more than 50% higher than that of the other two compositions. The similar dielectric response of copolymers with different compositions shown in the Figure 3-14 suggests that other mechanisms can compensate for the reduction of polarization response due to the crystallinity change. Reduction of the remnant polarization due to destruction of ferroelectric polarization ordering by the defect modification is one mechanism for compensation of polarization response in these compositions, as will be discussed in detail later.

Figure 3-14: Unipolar P-E loops of the P(VDF-CTFE) copolymers.
Figure 3-15 shows the comparison of the energy density between 15 and 20 wt% copolymers. As shown in the figure, because these two polymers possess a similar polarization response, the energy density of these two polymers is almost the same.

In the three compositions of P(VDF-CTFE) copolymers, the 15 wt% CTFE copolymer was found to exhibit the highest breakdown electric field. As already shown in Figure 3-5, the breakdown field of this polymer can be higher than 600MV/m. It is still not clear whether the high breakdown field of the 15 wt% CTFE copolymer is due to the intrinsic reason or the processing. Therefore, the highest measured energy density was obtained in the copolymer with 15 wt% CTFE.

3.3.2.7 Some discussions on P(VDF-CTFE) copolymers

A. Effect of CTFE on the dielectric properties of P(VDF-CTFE) copolymers
The above experimental results demonstrate that P(VDF-CTFE) copolymers are a group of materials with very high energy density. Therefore, it is important to understand how the comonomer CTFE affects the dielectric properties and energy density of copolymers. As already discussed in the previous study on P(VDF-TrFE-CFE) terpolymers, the bulky monomer after copolymerization with the PVDF-based polymer could be included, or excluded, or partially included in the crystalline phase.[27]

Previous studies showed that P(VDF-CTFE) copolymers with more than 20 mol% CTFE would be completely amorphous, which suggests that the crystalline phase could not accommodate a large amount of CTFE in PVDF lattice. Based on the patent from Solvay, in the polymerization process, VDF and CTFE monomers were fed into the reaction chamber at the beginning of polymerization.[20] Because of the different reactivity of VDF and CTFE, CTFE was used up much faster than VDF and a large amount of CTFE should be in the amorphous phase. The composition of the crystalline phase of these copolymers should be close to PVDF phase, but experimental results have shown that certain amount of CTFE was indeed included in the crystalline phases, which was manifested by the change of dielectric response and crystal structure with various compositions. DSC results also show that two crystalline phases, one nearly pure PVDF phase, whose melting temperature do not change with composition, and one CTFE modified PVDF phase, whose melting temperature decreases with CTFE, coexist in the P(VDF-CTFE) copolymers.

One direct effect of CTFE incorporation is reduction of crystallinity, which will reduce the maximum polarization response and energy density. However, it was found that for the P(VDF-CTFE) copolymers, the energy density of the three compositions is almost the same regardless of the reduction crystallinity. This means that other effects may compensate for the reduction of energy density due to the crystallinity change.

As already discussed above, copolymerization of CTFE with VDF may destruct the stability of ferroelectric domains and turn them into “nanodomains”, as proposed by simulation results using the \textit{ab initio} density functional theory.[28] The XRD result has shown the decrease of domain size with increasing CTFE in PVDF. Ferroelectric domains possess “critical size”, the domain size below which the macroscopic
ferroelectric domains will become unstable, analogous to PVDF-based relaxor ferroelectric polymers, as described in the proceeding chapter.[11,26,29] Under a high electric field, the nanodomains could be transformed into ferroelectric domains. After the field is removed, the ferroelectric domains can be converted back to nanodomains. Compared with the polarization response of ferroelectric domains, nanodomains possess much less remnant polarization, which will enhance the energy density of P(VDF-CTFE) copolymers because the energy density is determined by the difference between maximum polarization and remnant polarization.

The effectiveness of reduction of remnant polarization by CTFE incorporation can be further manifested by comparing the ratio of remnant polarization ($P_r$) to maximum polarization ($P_s$) between the PVDF homopolymer and P(VDF-CTFE) copolymers. Under an electric field of 250 MV/m, the $P_r / P_s$ of the copolymer (15 wt% CTFE) deduced from the data in Figure 3-13 is 0.46, in contrast to a much larger ratio of 0.70 for the PVDF homopolymer. Therefore, the enhancement of energy density by reduction of remnant polarization by CTFE could compensate the energy density loss due to the reduction of crystallinity. As a result, P(VDF-CTFE) copolymers of the three compositions studied have almost the same energy. From the crystal structure point of view, the transformation from nanodomain to ferroelectric domain corresponds to the reversible change between non-polar to polar conformations, which leads to lower remnant polarization.[30]

In addition to the reduction of remnant polarization due to the defect modification of the crystalline phase, the possible contribution from the crystalline-amorphous interphase may also improve the polarization response and energy density of the copolymers, which can compensate for the loss of energy density and reduction of polarization response due to the decrease of crystallinity with CTFE content. Experimental results have shown that in PVDF, the crystallinity could be greatly increased by applying an electric field.[31] It was proposed that the amorphous phase near the interphase between the amorphous and crystalline phases could be converted into the crystalline phase under an electric field. For P(VDF-CTFE) copolymers, due to
the reduction of crystal size with CTFE, the contribution from the amorphous-crystalline interface could be more and more significant.[32]

B. Dielectric nonlinearity of the P(VDF-CTFE) copolymers

The effective dielectric constant $K_{\text{eff}}$ with the applied field (i.e., $U_e = \frac{1}{2}K_{\text{eff}} \varepsilon_0 E^2$) of the copolymer with 15 wt% CTFE was calculated and is shown in Figure 3-16. Compared with the terpolymer, the copolymer shows much less nonlinear dielectric behavior. $K_{\text{eff}}$ of the copolymer shows very small variation (from 12 to 17) with the electric field in the range from zero electric field to 600MV/m. These experimental results verify the hypothesis proposed in the induction section of this chapter that a high dielectric constant may not be desirable to obtain high energy density due to a large field dependent dielectric nonlinearity resulting from a high dielectric constant. P(VDF-CTFE) copolymers, due to their low dielectric constant (~12-13), possess less nonlinearity and even under an electric field of around 600MV/m, the polarization response of these copolymers still does not show the polarization saturation effect, which is different from the P(VDF-TrFE-CFE) terpolymer. As a result, the energy density of P(VDF-CTFE) copolymers is much greater than that of the terpolymer. One tradeoff for materials with a

![Figure 3-16: Variation of the effective dielectric constant of the P(VDF-CTFE) copolymer (15 wt% CTFE) with the applied electric fields.](image)
small dielectric constant is that a very high electric field is required to obtain high energy density. Therefore, new materials, which have a dielectric constant in between those of terpolymers and copolymers, will be explored to obtain high energy density under a reasonable electric field. For example, for polymers with a dielectric constant of about 22, an electric field of only 500 MV/m is required to obtain an energy density of 25J/cm³.

3.3.3 Dielectric property and energy density of the P(VDF-HFP) (12 wt% HFP) copolymer

For P(VDF-HFP) copolymers, the effect of HFP on the properties of P(VDF-HFP) copolymers is very similar to the effect of CTFE on P(VDF-CTFE) copolymers.[33] The bulkier functional group –CF₃, compared with the chloride atom of CTFE, is more effective to modify the properties of P(VDF-HFP) copolymers. For example, the heat of fusion for the copolymer with 12 wt% (5.5 mol%) HFP is only about 21J/g and the melting temperature was reduced to 136°C. Accordingly, the remnant polarization of the copolymer is also reduced, as shown by the bipolar P-E loops of P(VDF-HFP) copolymers in Figure 3-17.

Figure 3-17: Comparison of Bipolar P-E loops between the P(VDF-HFP) copolymers with 10 and 12 wt% HFP.
Figure 3-18 shows the temperature dependence of the weak-field dielectric constant of the P(VDF-HFP) copolymer with 12 wt% HFP. The dielectric constant of the 12 wt% HFP copolymer is almost the same as that of the 10 wt% HFP copolymer. The dielectric constant at room temperature is about 12. Similar to the P(VDF-CTFE) copolymers, the loss peak around 80°C on the dielectric loss curve (1kHz, Figure 3-2(b)) almost disappears due to the increasing structural defects generated by incorporation of HFP in the polymer chains.

![Dielectric properties of P(VDF-HFP) copolymer](image)

Figure 3-18: Change of weak field dielectric properties of the P(VDF-HFP) (12 wt% HFP) copolymer

The unipolar P-E loops of unstretched 12 wt% HFP copolymer and the calculated energy density are shown in Figure 3-19. As a comparison, the energy density of the 10 wt% HFP copolymer is also shown in Figure 3-19(b). Although the crystallinity of the 12 wt% HFP copolymer is much lower than that of the 10 wt% HFP copolymer, its energy density is a little higher, which suggests that the effect of the reduction of remnant polarization surpasses that of the reduction of crystallinity. Under an electric field of 400 MV/m, an energy density of about 8 J/cm³ can be obtained.
In this chapter, P(VDF-CTFE) and P(VDF-HFP) copolymers were studied for candidate dielectric materials with very high energy density. These dielectric materials

![Graphs showing polarization and energy density](image)

Figure 3-19: (a) Unipolar P-E loops and (b) energy density of the P(VDF-HFP) (12 wt% HFP) copolymer, as a comparison, the energy density of the 10 wt% HFP copolymer is also shown in the figure.

### 3.4 Summary

In this chapter, P(VDF-CTFE) and P(VDF-HFP) copolymers were studied for candidate dielectric materials with very high energy density. These dielectric materials
possess a much lower dielectric constant (12-13) than the P(VDF-TrFE-CFE) terpolymer (about 55). For materials with certain maximum induced polarization, a low dielectric constant could avoid the “early polarization saturation”, i.e., the induced polarization of dielectric materials reaches the maximum under an electric field much below the breakdown field. Therefore, very high energy density (larger than 24J/cm³) can be obtained in P(VDF-CTFE) and P(VDF-HFP) copolymers. From the structural point of view, bulky comonomers HFP and CTFE act as defects in the crystal structure of PVDF, just like the role of CFE in the P(VDF-TrFE-CFE) terpolymer. These defects can expand the interchain space of the crystalline phase and stabilize the nonpolar phase, as observed from the FTIR data.

Incorporation of HFP and CTFE into the polymer was also found to greatly reduce the crystallinity of the polymers, as seen from the DSC, which will reduce the energy density. The reduction of remnant polarization by the defect modification could compensate the energy density loss due to reduction of crystallinity. Therefore, the P(VDF-CTFE) and P(VDF-HFP) copolymers with different compositions exhibit almost the same energy density. From the XRD results, the ferroelectric domain size was observed to be reduced by defect modification and the ferroelectric domains probably become “nanodomains”, which will reduce the remnant polarization. From the crystal structure point of view, the reduction of remnant polarization was thought to be associated with the destruction of the polar phase due the incorporation of CTFE and HFP. Compared with the PVDF homopolymer, these polymers show much less polarization hysteresis which can reduce the energy loss for capacitor applications.

References

[23] H. S. Xu, G. Shanthi, V. Bharti, Q. M. Zhang, Macromolecules, 2000, 33, 4125
Chapter 4

Dielectric Properties of the PVDF-based Terpolymer/copolymer and Terpolymer/PMMA Blends

4.1 Introduction

The last two chapters presented the development and characterization of PVDF-based terpolymers and copolymers for energy storage capacitor applications. P(VDF-TrFE-CFE) terpolymers possess a high dielectric constant (about 55 at 1 kHz) at room temperature and were shown to be dielectric materials with an energy density larger than 9 J/cm$^3$. For P(VDF-CTFE) copolymers with a dielectric constant of ~12 at 1 kHz at room temperature, very high energy density (>24 J/cm$^3$) can be obtained. The discovery of high energy density with a fast discharge speed in P(VDF-CTFE) copolymers represents a breakthrough in high energy density capacitor materials.

Polymer blends, which exploit the merits of both the base polymer and the additive polymer, offer a great opportunity to improve and tailor the properties of the base polymer. Previous works have shown that polymer blends with properly selected compositions and processing conditions can remarkably alter or improve the mechanical, electromechanical, and electro-optical properties of the materials.[1-6] For example, the electromechanical response of the P(VDF-TrFE)/P(VDF-CTFE) polymer blends were studied by Z. Li, et al., and these blends are found to be promising for electromechanical applications.[1] After the P(VDF-TrFE-CFE) terpolymer is blended with a small amount of poly(methyl methacrylate) (PMMA), the mechanical properties of the P(VDF-TrFE-CFE) terpolymer can be enhanced without too significantly reducing the strain level. Therefore, the elastic energy density is improved.[2] The terpolymer/PMMA blend represents another good example that blend can improve the properties of the base polymer.
In this chapter, the blends of P(VDF-TrFE-CFE) terpolymer and P(VDF-CTFE) copolymer, which are both semicrystalline polymers, will be investigated. Since the miscibility of the two polymers is still unknown, it will be studied first. Because the dielectric constant of the terpolymer is about 55 (1 kHz) and that of the copolymer is about 12 (1 kHz) at room temperature, it can be expected that the dielectric constant of the polymer blends can be tunable from 12 to 55 with different blend compositions. The energy density is another important parameter for dielectric materials. The high field dielectric properties and energy density of the blends will be further studied in this chapter. In addition to the P(VDF-TrFE-CFE)/P(VDF-CTFE) blends, P(VDF-TrFE-CFE)/PMMA blends were also studied, and the dielectric properties of these blends will be presented.

4.2 Experimental

Two methods were employed to prepare laboratory scale blend samples: solution cast and microcompounding methods. For the PVDF terpolymer/ P(VDF-CTFE) copolymer blends, depending on the compositions, either the solution cast method or microcompounding method was used. For blends with low P(VDF-CTFE) content (terpolymer-rich blends), i.e., 0, 5, 10, 15 and 20 wt% copolymer, it was found that the solution cast method was quite effective to produce high quality films. The PVDF terpolymer (P(VDF-TrFE-CFE) 63/37/7.5 mol%) and copolymer (P(VDF-CTFE) 91/9 mol% or 85/15 wt%) were dissolved in N, N-Dimethylformamide (DMF) or 2-Butene (MEK). The terpolymer and copolymer solutions were mixed together by proper ratio determined by the required blend compositions. The PVDF terpolymer/copolymer solution mixtures were poured on glass slides and dried at 70°C for 5 hrs. After the solution was dried, the blend films (with an approximate thickness between 12 and 20 µm) were peeled off the glass slides and further annealed at 120-140°C for 10 hrs. in a vacuum oven to improve the crystallinity and remove the residual solvent. For blends with a high concentration of the copolymer (50, 80, 85, 90 and 95 wt% copolymer,
copolymerrich blends), the solution cast method is not suitable because the breakdown field of the blend films prepared by this method is low and the conduction loss is high. They were mixed in a micro-compounder (Haake Minilab, Thermo Electro Corporation) at a speed of 150 rpm under 180°C for half an hour. The blend films were then obtained by compression molding. The film thickness is between 30-50 µm.

The PVDF terpolymer/PMMA blends were prepared by the solution casting method using the same procedures as were used to prepare the terpolymer-rich terpolymer/copolymer blends. The compositions of the PVDF terpolymer/PMMA blends are 0, 1.5, 2.5 and 5 wt% PMMA.

The procedures for electrode deposition and electrical measurement have been described in Chapter 2.[7] They will not be repeated here.

The glass-transition temperature, melting point, crystallization temperature and crystallinity of the blends were studied by the differential scanning calorimetry (DSC, TA Q100). The mechanical properties of the blends were measured by a dynamic mechanical analyzer (DMA, TA2980). The microstructure of the blends was studied by Scanning Electron Microscopy (SEM, Hitachi S-3000H).

4.3 Results and discussions

4.3.1 P(VDF-TrFE-CFE) terpolymer/P(VDF-CTFE) copolymer blends

4.3.1.1 Miscibility Study

When two polymers are mixed together, the change of Gibbs free energy $\Delta G_m$ can be expressed by the Flory-Huggins equation:[8]

$$\Delta G_m = RT \left[ n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12} \right]$$

4.1
where $R$ is the gas constant; $T$ is the temperature; $n_i$ and $\phi_i$ ($i=1$ or 2) are the moles and volume fraction of the polymers; and $\chi_{12}$ is a parameter related to the interaction between the two polymers. In most cases, the absolute value of the mixing entropy (the first two terms, always negative) is very small due to the long chain of the polymer and the enthalpy is always positive; consequently, $\Delta G_m$ is positive for most polymer blends. Hence, most polymers are not miscible unless strong interactions, such as hydrogen bond, exist between the polymers.

The interaction parameter can be calculated directly from the solubility parameter $\delta$ by the following equation:

$$\chi_{12} = V_r^* (\delta_1 - \delta_2)^2 / RT \tag{4.2}$$

where $V_r$ is the reference volume. The solubility parameter of the polymers can be further deduced by the group contribution method:

$$\delta = \Sigma F_i^*/\Sigma V_i^* \text{ (cal.cm}^{-3})^{0.5} \tag{4.3}$$

$F_i^*$ is the molar attraction constant of the $i^{th}$ group and $V_i^*$ is the corresponding molar volume constant of the group.

$F_i^*$ and $V_i^*$ of the groups for calculating the solubility parameter of the PVDF terpolymer and copolymer are listed in Table 4-1. The solubility parameters of the terpolymer and copolymer calculated by Eq. 4.3 are 6.99 and 6.34 (cal.cm$^{-3}$)$^{0.5}$, respectively. Using the solubility parameters, the interaction parameter can be estimated using Eq. 4.2. In the calculation, the $RT$ at room temperature is $\sim$600 cal/mol and $V_r$ is $\sim$100 cm$^3$/mol. The estimated $\chi_{12}$ is 0.07. Normally for two polymers without other strong interaction forces, such as hydrogen bond, to ensure the miscibility, the critical $\chi$ should be less than 0.002.[9] Therefore, it is possible that the PVDF terpolymer and copolymer may not be completely miscible although the chemical compositions of terpolymers and copolymers are similar.
Table 4-1: Molar volume and attraction constants of related groups for the PVDF-based terpolymer and copolymer.[8]

<table>
<thead>
<tr>
<th>Group</th>
<th>Molar volume constant $V^*$ (cm$^3$.mol$^{-1}$)</th>
<th>Molar attraction constant $F^*$ (cal.cm$^3$)$^{0.5}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$-</td>
<td>16.5</td>
<td>132</td>
</tr>
<tr>
<td>-CF$_2$-</td>
<td>32.1</td>
<td>159.95</td>
</tr>
<tr>
<td>&gt;CH-</td>
<td>1.9</td>
<td>23</td>
</tr>
<tr>
<td>-F</td>
<td>10.8</td>
<td>167.832</td>
</tr>
<tr>
<td>&gt;C&lt;</td>
<td>-14.8</td>
<td>-97</td>
</tr>
<tr>
<td>-Cl</td>
<td>23.9</td>
<td>264</td>
</tr>
</tbody>
</table>

One criterion which can be used to judge the miscibility of the two polymers is the separation of glass transition of the two polymers. After two immiscible polymers are mixed together, two separate glass transition temperatures can be observed. If one glass transition temperature is observed, the two polymers are possibly miscible.

Because the glass transition of the terpolymer and copolymer could not be easily separated from the DSC data, DMA was used to evaluate the miscibility of the two polymers. Figure 4-1 shows the mechanical loss tangent at 2 Hz of the terpolymer, the copolymer and the blends of various compositions. Two relaxation peaks can be observed in the terpolymer. The first relaxation process at about -10°C is related to the glass transition.[2,10] The second strong relaxation occurs around 20°C. This relaxation is probably related to some relaxation processes in the crystalline phase or crystalline/amorphous interphases because the dielectric constant maxima occur around this temperature and the very large dielectric constant in the PVDF terpolymer comes mainly from the crystalline phase. Analogously, below 60°C, two relaxation peaks are also observed in the P(VDF-CTFE) copolymer. The first peak around -30°C is related to the glass transition, similar to the PVDF homopolymer.[11-13]
For the blend with the 50 wt% copolymer, as seen in Figure 4-1(a), a relaxation peak corresponding to the glass transition of the P(VDF-CTFE) copolymer can be clearly observed. In addition to this peak, a new relaxation peak can be found at around -20°C. The glass transition of the terpolymer cannot be observed on this curve, probably because the relaxation peak is so weak and overlaps with other peaks. On the other hand, for blends with a small amount of the copolymer (5 wt% to 15 wt% copolymer), the glass transition of the terpolymer can be clearly seen on the curves. However, the shift of the
glass transition temperature with the addition of the copolymer cannot be determined unambiguously because the peaks are broad. For a blend with the 95 wt% copolymer, a peak corresponding to the glass transition of the copolymer can be observed, as shown in Figure 4-1(b). A shift of the peak position about 3°C to a higher temperature can be discerned (from about -30°C to about -27°C). For a blend with the 85 wt% copolymer, the glass transition of the copolymer can still be discernable, but it is not clear due to the overlap with other possible new relaxation processes. The above results show that, in the terpolymer and copolymer blends, in addition to their respective glass transition temperatures, a new relaxation between the glass transitions of the two polymers, which may result from the solid solution of the two polymers, can be observed. This suggests that the PVDF terpolymer and copolymer can only be partially miscible. This is consistent with the prediction, based on their interaction parameters, that the two polymers may not be completely miscible.

The melting temperature of the blends was studied by DSC and the result (second cycle) is shown in Figure 4-2(a). In the semicrystalline polymer blends, the possibility that the two polymers will co-crystallize is very small. The DSC results show that the blends have two separate main melting peaks, which correspond to the melting of the terpolymer, below 130°C, and that of the copolymer, around 165°C. Even with a small amount of the terpolymer in the copolymer or a small amount of the copolymer in the terpolymer, these two peaks can be clearly observed. Table 4-2 summarizes the total heat of melting, which is the total area of the melting peaks of the terpolymer and copolymer in the blends; the respective heat of melting of the terpolymer and copolymer; and the normalized heat of melting of the terpolymer and copolymer (the actual heat of melting of each component divided by the weight ratio) in the terpolymer-rich the blends (the heat of melting was from the first cycle of DSC). The total heat of melting increases slightly as the copolymer is added to the blends. The heat of melting of the copolymer component in the blends is greater than 50 J/g, much larger than that of the pure copolymer, which is less than 21 J/g. The tradeoff is the small reduction of crystallinity of the terpolymer (less than 10% for blends with <15 wt% copolymer). This result suggests that there exists a certain degree of interaction between the copolymer and the
Figure 4-2: (a) DSC of the terpolymer/copolymer blends around melting temperatures (b) upper glass transition temperatures of blends and (c) $(T_m^0 - T_m)$ vs. $\phi_1^2$ of the blends.
terpolymer during the crystallization process. Through this interaction, the crystallinity of the copolymer component is greatly increased. One possible reason for this phenomenon is that because the terpolymer has a lower melting temperature than does the copolymer, during the annealing process the terpolymer may facilitate the crystallization of the copolymer.

Table 4-2: Summary of the heat of melting of the terpolymer-rich blends

<table>
<thead>
<tr>
<th>Compositions (terpolymer/copolymer)</th>
<th>Total heat of melting (J/g)</th>
<th>Heat of melting of terpolymer component (J/g)</th>
<th>Heat of melting of copolymer component (J/g)</th>
<th>Normalized heat of melting of terpolymer component (J/g)</th>
<th>Normalized heat of melting of copolymer component (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>21.1</td>
<td>21.1</td>
<td>0</td>
<td>21.1</td>
<td>0</td>
</tr>
<tr>
<td>95/5</td>
<td>22.4</td>
<td>19.5</td>
<td>2.9</td>
<td>20.6</td>
<td>57.8</td>
</tr>
<tr>
<td>90/10</td>
<td>23.2</td>
<td>17.7</td>
<td>5.5</td>
<td>19.7</td>
<td>54.9</td>
</tr>
<tr>
<td>85/15</td>
<td>24.5</td>
<td>17.0</td>
<td>7.5</td>
<td>20.0</td>
<td>50.2</td>
</tr>
<tr>
<td>80/20</td>
<td>24.8</td>
<td>14.2</td>
<td>10.6</td>
<td>17.7</td>
<td>53.0</td>
</tr>
</tbody>
</table>

The slight but continuous reduction of melting temperature with increasing copolymer content is another indication of the partial miscibility of the blends. The reduction of the melting temperature of the terpolymer in the blend can be attributed to the interaction between the terpolymer and copolymer. For miscible polymer blends, suppression of the melting temperature can be fitted by the following equation[14,15]:

\[
T_m^o - T_m = -T_m^o B^* V_{2u} \phi_1^2 / \Delta H_{2u}
\]

In this equation, \( T_m^o \) is the melting temperature of the terpolymer; \( T_m \) is the melting temperature of the blends; \( B \) is the interaction energy; \( \Delta H_{2u} / V_{2u} \) is the heat of fusion per unit volume; and \( \phi_1 \) is the volume fraction of the copolymer. The data fitting result is shown in Figure 4-2(c). \(( T_m^o - T_m ) \) vs \( \phi_1^2 \) is not a linear relation, probably because the two
polymers are partially miscible and the compositions used for fitting are not the real composition of the amorphous phases. The experimental results from DSC indicate that even though the two polymers have a low degree of miscibility, they do have some degree of interaction during the crystallization process which can affect the crystallinity and crystalline morphology.

From DSC, one glass transition-like process can also be observed at a temperature higher than zero degree for both polymers, as shown in Figure 4-2(b). It has been reported that in PVDF-based semicrystalline polymers, two glass transition temperatures were frequently observed. The glass transition temperature at a higher temperature (which was named the upper glass transition temperature, about 40°C) was thought to be related to the amorphous phase around the crystalline region.[16,17] In this study, the glass transition-like behavior below 20°C for the terpolymer and around 45°C for the copolymer should be attributed to the relaxation of the amorphous phase around the crystalline phase. The transition temperatures of the terpolymer and copolymer do not change in the blends compared with neat polymers, as seen in the figure, which suggests that the interface between the crystalline and amorphous phases is not modified for both the terpolymer and copolymer components in the blends.

Though experimental results from DSC and DMA may suggest a small degree of miscibility between the copolymer and terpolymer, the phase separation in the blends was observed directly by SEM. Figure 4-3 shows the intersection images of the copolymer-rich blends with 85 and 95 wt% copolymer. Before these images were taken, the blend samples were immersed into MEK solvent for 5-10 seconds to remove the terpolymer. The copolymer cannot be dissolved in the MEK. From the SEM images of the intersection, for the 5 wt% terpolymer blend, only separate cavities, where the terpolymer was removed, were observed; whereas for the 15 wt% terpolymer blend, the deep cavities form continuous phases, which suggests that the terpolymer forms a continuous phase in the copolymer matrix. Like many other immiscible polymer blends, in PVDF terpolymer and copolymer blends, the morphologies of the additive polymer change from separate phase to continuous phase in the polymer matrix with the increasing concentration of the additive polymer.
4.3.1.2 Weak-field and high-field dielectric Properties

Figure 4-4(a) shows the weak field dielectric constant of blends with various compositions. As expected, addition of the copolymer in the terpolymer results in a decrease of the dielectric constant due to the lower dielectric constant of the copolymer film, about 12 at 1 kHz, in comparison with about 55 of the terpolymer, as also shown in Figure 4(a). Because of the lower dielectric loss of the copolymer, the dielectric loss of the blends is also reduced by mixing the terpolymer with the copolymer, especially under high frequency range, as shown in Figure 4-4(b). For the copolymer-rich blends, the results are just the opposite: addition of the terpolymer increases the dielectric constant as well as the dielectric loss, as shown in Figure 4-4(c) and (d).

The temperature dependence of the dielectric constant and loss for terpolymer-rich blends at 1 kHz are shown in Figure 4-5. In the measurement temperature range, the dielectric constant and dielectric loss of the blends decrease with addition of the copolymer. The temperature of dielectric maximum does not change with the addition of the copolymer.
Figure 4-4: (a) Weak field dielectric constant of terpolymer-rich blends (b) dielectric loss of terpolymer-rich blends (c) weak field dielectric constant of copolymer-rich blends (d) dielectric loss of copolymer-rich blends.

Figure 4-5: Temperature dependence of weak field dielectric constant and dielectric loss of terpolymer-rich blends at 1 kHz.
The high field dielectric property of the blends was characterized by measuring the unipolar P-E loops, which are shown in Figure 4-6. For blends with a high concentration of the copolymer, the polarization was reduced greatly by adding the 15 and 20 wt% copolymer. This occurs because when the applied electric field is less than 400 MV/m, under the same electric field, the polarization response of the copolymer is much lower than that of the terpolymer, which is also shown in the figure. The blends with the 5 and 10 wt% copolymer, however, exhibit anomalous dielectric behavior. For example, for blends with the 10 wt% copolymer, under a low electric field (<165 MV/m), the polarization level is still lower than that of the terpolymer, but above 165 MV/m, as shown in Figure 4-6(a), the polarization of the blend exceeds that of the terpolymer. It can also be observed that for the 5 and 10 wt% blends, the maximum induced polarization level is higher than that of the pure terpolymer. As shown in Figure 4-6(b), the maximum polarization of the blend with the 10 wt% copolymer is 0.115 C/m² and that of the blend with the 5 wt% copolymer is also higher than 0.1 C/m². The polarization of the terpolymer was found to never exceed 0.1 C/m². The results of the blends with the 5 and 10 wt% copolymer suggest that the interaction between the two polymers raises the polarization level of the blends beyond that of the terpolymer.

Figure 4-6: Unipolar P-E loops of terpolymer-rich P(VDF-TrFE-CFE) terpolymer/P(VDF-CTFE) copolymer blends (a) under an electric field of 250MV/m and (b) under highest applied electric field.
The crystallinity change of the blends was considered to be one of the possible mechanisms for the polarization enhancement because the induced polarization in the ferroelectric polymer under an electric field comes mainly from the crystalline phases. As already shown in Table 4-2, by increasing amount of the copolymer, the heat of melting and the crystallinity of the blends are increased. The crystallinity increase comes mainly from the contribution of the copolymer component in the blend, and the crystallinity of the terpolymer component tends to decrease in the blend. Although the crystallinity of the copolymer component in the blends is much higher than that of the pure copolymer (about two times that of pure copolymer) and its polarization level may be greatly enhanced, from the reduction of the polarization in the blends with the 15 and 20 wt% copolymer, we may conclude that its polarization is still much lower than that of the terpolymer. Therefore, the crystallinity increase could partially compensate for the polarization loss of the blends after adding the copolymer with lower dielectric response, but this is not the only compensation mechanism.

The crystal structure of the crystalline phase in PVDF-based polymers is known to be sensitive to processing.[13] Different processing conditions can lead to different ratios of TG, all-trans and T3G conformations, which will affect the dielectric response of the polymers. In some cases, this may lead to the enhancement of the high field dielectric response. For example, in the PVDF terpolymer, more all-trans conformation may improve the dielectric response because all-trans conformation has higher dipole density than other conformations have. As already seen from the DSC results, the terpolymer and copolymer have a certain interaction and the crystal structure of the two components in the blends may change.

The microstructure of the blends was examined by XRD. As shown in Figure 4-7, no noticeable structure change in the terpolymer-rich blend can be observed. The peak positions for the terpolymer component in the blend do not change in comparison with the pure terpolymer. The diffraction peak for the copolymer cannot be observed on the figure due to the very low diffraction intensity of the copolymer. Similarly, for the copolymer-rich blends, the peak positions of the copolymer and terpolymer are also kept at the same positions as those of the pure copolymers. Therefore, no obvious structural
change of the terpolymer and copolymer components in the blends can be observed. However, we cannot exclude the possible minor structural change, and XRD is not sensitive enough to detect this change. As will be discussed in the next chapter on the enhancement of dielectric properties in nanocomposites, the minor structural change may have a great impact on the dielectric response under a high electric field, especially for the P(VDF-TrFE-CFE) terpolymer, whose dielectric response is sensitive to structural change.

The most possible mechanism for the polarization enhancement is the contribution from the interfaces between these two polymer components. Several reports on PVDF/Nylon blends and 2-2 composites showed that blends and composites prepared by certain processing and with suitable compositions could generate a higher polarization response than both pure PVDF and Nylon.[4,18-20] This phenomenon obviously contradicts the mixing rule of the composite materials. An additional polarization contribution from the interfaces was proposed in these multi-component systems and the experimental data could be fitted by taking account of this interfacial polarization, but the origin of the interfacial polarization is still unclear.

Figure 4-7: XRD patterns of P(VDF-TrFE-CFE) terpolymer/P(VDF-CTFE) copolymer blends
From the experimental results of terpolymer-rich blends, we notice that the dielectric anomalies occur only in the blends with a small amount of the additive polymer. For example, addition of more than 15 wt% copolymer in the terpolymer leads to a greatly reduced polarization. This may suggest that the dielectric anomalies of the blends are an interface-related phenomenon. As already shown in Figure 4-3, with an increasing amount of the additive polymer, the morphologies of additive polymer will change from separate phase to continuous phase in the base polymer. The separate droplet-like morphology can have a higher ratio of interface area between these two polymers than the continuous morphology. Therefore, a higher content of the additive polymer tends to destruct the interfacial effect.

For the copolymer-rich blends, on the other hand, it is found that addition of a small amount of the terpolymer will reduce the polarization response of the blends. Figure 4-8 shows the unipolar P-E loops of the copolymer-rich blends. It is very interesting that for the blends with a small amount of the terpolymer, the induced polarization is smaller than that of the pure copolymer although the polarization of the terpolymer is much higher than that of the copolymer under the same electric field. This result further suggests that the dielectric anomalies of the blends may be interface-related phenomenon.

![Figure 4-8: Unipolar P-E loops of copolymer-rich PVDF terpolymer/P(VDF-CTFE) copolymer blends](image)
This interfacial effect should be directly related to the properties of the base and additive polymers. Depending on which polymer is the base material, the interfacial effect may enhance or reduce the dielectric response, as manifested by the experimental results of terpolymer-rich and copolymer-rich blends, but it is not clear what the determinant factor for this interfacial effect is.

In terpolymer-rich blends, we should notice that the polarization enhancement is the field-dependence phenomenon. Under a low electric field, the polarization of the blends is lower than that of the terpolymer, and the anomaly happens under a high electric field. Another observation is the change of dielectric nonlinearity, as seen from the P-E loops. For example, even with a small amount of the copolymer (5 wt%) in the terpolymer, as seen in Figure 4-6, the field dependent nonlinear dielectric response is changed greatly. The P-E loops of 5 and 10 wt% blends tend to be more linear. The apparent nonlinearity change may be caused by the possible structural change (probably around the interface) or other reasons (for example, conduction).

4.3.1.3 Breakdown field of the PVDF terpolymer/copolymer blends

Addition of a small amount of the copolymer into the terpolymer can greatly improve the breakdown field, which is very important for high voltage application of dielectric materials. Higher breakdown means a higher working field or higher reliability when the dielectric materials are applied to the same electric field. Figure 4-9 shows the comparison of the breakdown test results of the terpolymer and the blend with the 5 wt% copolymer. The breakdown results were analyzed by Weibull analysis:[21]

\[
\ln(\ln\left(\frac{1}{1-F(x)}\right)) = \beta \ln(\alpha) - \beta \ln(x)
\]

4.5

In this equation, F(x) is the cumulative failure of test samples, E is the measured breakdown electric field, \(\beta\) is the shape parameter and \(\alpha\) is the characteristic breakdown strength (63.2% of accumulated probability of breakdown). As shown in the figure, the characteristic breakdown field of the blend was improved by about 100 MV/m, compared
with that of the pure terpolymer. For real dielectric materials, due to the processing and other reasons, defects exist which can significantly reduce the breakdown field of the dielectric materials. This leads to the deviation of the real breakdown field from the theoretical breakdown field. When the samples are prepared in the same conditions, the defects in the terpolymer and its blends should have the same statistic distribution; therefore the breakdown fields of the neat terpolymer and its blends should have similar statistic distribution. As shown in Figure 4-9, the shape parameters $\beta$ are almost the same in the neat terpolymer and its blend. Improvement of the characteristic breakdown field of the blend should not result from the change of the statistic distribution of the measured breakdown fields, but from the improvement of the intrinsic breakdown field of the blend.

![Figure 4-9: Comparison of the breakdown fields of the terpolymer and the blend with 5 wt% P(VDF-CTFE) copolymer](image)

Several mechanisms govern the dielectric breakdown of the polymer; one of these is the electromechanical breakdown mechanism.\[22\] The main mechanism for the improvement of the dielectric breakdown field in the blends is thought to be caused by the increase of mechanical properties of the terpolymer, as shown in Figure 4-10, the
DMA results of the terpolymer, copolymer and their blends. Because the storage modulus of the copolymer is higher than that of the terpolymer and in the blend the entanglement of the terpolymer and copolymer chains is inevitable, addition of the copolymer into the terpolymer improves the modulus of the terpolymer (about 50% higher). The breakdown field $V_{em}$ (Stalk and Garton model) of the dielectrics can be expressed as:[22]

$$V_{em} = d_0 \left( \frac{Y}{\varepsilon_0 \varepsilon_r \exp(1)} \right)^{\frac{1}{2}}$$  \hspace{4cm} (4.6)$$

where $d_0$ is the thickness of the dielectrics; $Y$ is the modulus of the polymer; $\varepsilon_0$ is the dielectric constant of the vacuum; and $\varepsilon_r$ is the relative dielectric constant of the dielectrics. In this equation, the breakdown field of the dielectrics is inversely proportional to the square root of the high field dielectric constant (for nonlinear dielectric materials, the high field dielectric constant can be quite different from the weak field dielectric constant) and is proportional to the square root mechanical modulus. The high field dielectric constant can be calculated from the slope of the P-E loops. For blends with the 5 and 10 wt% copolymer, the high field dielectric constant is almost the same or even higher than that of the neat terpolymer. It is obvious that improvement of

Figure 4-10: Storage modulus of the terpolymer, the P(VDF-CTFE) copolymer and their blends
the modulus increases the breakdown field of the blends. It should be noted that the 5 wt% copolymer is enough to improve the modulus by 50% and that the modulus of the blend with 15 wt% copolymer is almost the same as that of the blend with 5 wt% copolymer probably as a result of the partial miscibility between the terpolymer and copolymer.

The dielectric contrast between the terpolymer and copolymer is another factor that improves the breakdown field of the blends with a small amount of the copolymer. Because the dielectric constant of the terpolymer is 2-4 times that of the copolymer, the electric field will be concentrated in the copolymer and mitigated in the terpolymer. At the same time, the copolymer is a polymer with a very high breakdown field. The breakdown field of the blends can therefore be improved.

4.3.1.4 Energy density of PVDF terpolymer/copolymer blends

Energy density of the terpolymer-rich blends was calculated from the unipolar P-E loops shown in Figure 4-6. Improvement of the breakdown field and enhancement of the dielectric response result in improvement of energy density for blends with a small amount of the copolymer, as shown in Figure 4-11. The maximum energy density of the

![Energy density of the terpolymer-rich blends](image_url)
blend with 10 wt% copolymer can be 11.5 J/cm$^3$, which is much larger than the maximum energy density obtained by the neat polymer (about 9 J/cm$^3$).

### 4.3.2 PVDF Terpolymer/PMMA blends

PVDF-based polymers and poly(methyl methacrylate) (PMMA) blends have been studied for more than thirty years.[23-28] PVDF-based polymer/PMMA blends were thought to be miscible in all the compositions at a usual procession temperature range because the additional contribution to mixing enthalpy from the hydrogen bond formed between the PVDF-based polymer and PMMA. Miscibility and the electromechanical properties of the PVDF terpolymer and PMMA have been investigated, and improvement of the electromechanical properties of the PVDF terpolymer by blending with PMMA has been observed due to the increase of mechanical properties in the blends.[2] Here, further experimental results of the PVDF terpolymer/PMMA blends for dielectric application will be presented.

P(VDF-TrFE-CFE)/ PMMA blends with a small amount of PMMA (up to 5 wt%) were investigated. Figure 4-12(a) shows the dependence of the dielectric constant on temperature at 1 kHz of the blends with various compositions. A continuous decrease of the dielectric constant of the blends with an increasing amount of PMMA can be observed on the figure. At room temperature, the dielectric constant of the blends decreases almost linearly with PMMA content. For the blend with 5 wt% PMMA, the dielectric constant is about two thirds that of the pure terpolymer.

PMMA is an amorphous polymer with a lower dielectric constant (about 3.2 at 1 kHz at room temperature), much higher glass transition (about 105°C) and a higher Young’s modulus (>1800 MPa) than the terpolymer.[29,30] PMMA and the PVDF-based polymer are miscible in the amorphous phase, and PMMA is not included in the crystalline phase. One significant effect of adding PMMA into PVDF-based polymers is the large reduction of crystallinity. For the terpolymer and PMMA blends, the heat of melting changes from about 21 J/g for the pure terpolymer to 20 and 18.5 J/g for blends with 2.5 and 5 wt% PMMA, respectively. Because the dielectric constant of PMMA is
much lower than that of the terpolymer and PMMA only exists in the amorphous phase, the contribution of PMMA to the dielectric constant is very small. The dielectric response of the terpolymer and the blends comes mainly from the crystalline phase of the

Figure 4-12: (a) Temperature dependence of the dielectric constant of P(VDF-TrFE-CFE) terpolymer/PMMA blends (b) reduction of crystallinity, room temperature dielectric constant and polarization level (at 250 MV/m) with PMMA content
terpolymer. However, as shown in Figure 4-12(b), the decrease of the dielectric constant at room temperature is much faster than the decrease of crystallinity, which indicates that the reduction of crystallinity is only one factor that results in the reduction of the dielectric constant.

From Figure 4-12(a), the shift of the dielectric maxima to a higher temperature with PMMA can be noticed. A similar phenomenon was also observed in electron irradiated PVDF-TrFE/PMMA blends.[28] It was thought that although PMMA was in the amorphous phase, it might influence the interface between the crystalline and amorphous phases. PMMA, which has a much higher glass transition temperature than does the terpolymer, may retard the chain movement of the terpolymer and dipole orientation, leading to a lower dielectric constant.

Figure 4-13 shows the unipolar P-E loops of the terpolymer and blends with different compositions. Corresponding to the decrease of the weak field dielectric constant, the induced polarization was reduced by adding PMMA into the terpolymer. The decrease of polarization is still faster than crystallinity change, but a little slower than the weak field dielectric constant, which suggests the retarding effect may be mitigated by the electric field or due to the frequency dependence effect (the frequency for the P-E measurement is 10 Hz).

![Unipolar P-E loops of P(VDF-TrFE-CFE) terpolymer/PMMA blends](image)

Figure 4-13: Unipolar P-E loops of P(VDF-TrFE-CFE) terpolymer/PMMA blends
Another effect of PMMA addition is the improvement of the mechanical property of the terpolymer. The storage modulus of the blends with 1.5 and 5 wt% PMMA is shown in Figure 4-14. The modulus of the blends is increased with PMMA content. The increase of the glass transition temperature and entanglement of the polymer chain of the terpolymer and PMMA are two reasons for the improvement of storage modulus in the blends.

![Storage Modulus vs Temperature](image)

Figure 4-14: Storage modulus of P(VDF-TrFE-CFE) terpolymer/PMMA blends

Similar to the case of the P(VDF-TrFE-CFE) terpolymer/P(VDF-CTFE) copolymer blends, improvement of mechanical properties leads to a higher breakdown field. The Weibull analysis of the breakdown test results is shown in Figure 4-15. The breakdown field of the 2.5 wt% blend is 314 MV/m (the dielectric breakdown field of the terpolymer prepared under the same condition is 280 MV/m, shown in Chapter 2), about 30 MV/m higher than that of the pure terpolymer.

The energy density of the terpolymer/PMMA blends is shown in Figure 4-16. For blends with a small amount of PMMA (1.5 and 2.5 wt%), the energy density is nearly the same as for the pure terpolymer. The energy density starts to decrease when the PMMA content is raised to 5 wt%. Although the polarization response of the blends decreases with PMMA content, as shown in Figure 4-13, due to lesser dielectric nonlinearity of the
blends, the energy density of the blends with low PMMA content is nearly the same as that of the neat terpolymer.

Figure 4-15: Weibull analysis of the breakdown field of P(VDF-TrFE-CFE) terpolymer/PMMA (2.5 wt% PMMA) blends ($\alpha=314$ MV/m, $\beta=3.47$)

Figure 4-16: Energy density of P(VDF-TrFE-CFE) terpolymer/PMMA blends
4.4 Conclusions

In this chapter, the experimental results of two polymer blend systems, including P(VDF-TrFE-CFE)/P(VDF-CTFE) and P(VDF-TrFE-CFE)/PMMA blends, were presented.

For P(VDF-TrFE-CFE) terpolymer /P(VDF-CTFE) copolymer blends, the solubility parameters of the copolymer and terpolymer were determined. Based on the solubility parameters, it was expected that the two polymers might not be completely miscible. Experimental results of DMA, DSC and SEM show some signs of small degree of miscibility between the two polymers, i.e., the P(VDF-TrFE-CFE) terpolymer and P(VDF-CTFE) copolymer can be partially miscible.

The weak field dielectric constant of the blends can be tuned in a wide range from around 55, the dielectric constant of the terpolymer, to 12, the dielectric constant of copolymer. The high field dielectric properties of the blends exhibit anomalous behavior. For blends with a small amount of the copolymer in the terpolymer or small amount of the terpolymer in the copolymer, the dielectric response seems to not obey the general mixing rule of composites. The polarization of the composites was enhanced by adding a polymer of low dielectric response and reduced by adding a polymer of high dielectric response. The anomalous dielectric response in the blends was thought to mainly originate from the interfacial effect between these two polymers. Too much additive polymer may destruct the interfaces and reduce the contribution of the interfacial effect.

Due to improvement of the storage modulus of the blends and the less concentrated electric field in the terpolymer, the breakdown field of the terpolymer-rich blends was improved by adding a small amount of copolymer, compared with that of the pure terpolymer. A higher breakdown field and higher induced polarization level result in higher energy density in the terpolymer-rich blends.

The P(VDF-TrFE-CFE) terpolymer and PMMA polymer are completely miscible in the amorphous phase. Due to the much higher storage modulus of PMMA, the modulus of P(VDF-TrFE-CFE)/PMMA blends were improved and the breakdown field of the blends was also increased. Because of the lower dielectric response of PMMA, the
dielectric constant of the blends was reduced by adding PMMA. For a small amount of PMMA addition (<2.5 wt%), the energy density of the blend is almost the same as that of the pure terpolymer, but a higher breakdown field can be obtained in these blends.

In summary, in this chapter, various blends were studied. The blends with suitable compositions were able to improve the energy storage ability of polymers.

References

Chapter 5

Enhancement in Polarization Response and Energy Density of Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) Terpolymer by the Interface Effect in the Nanocomposites

5.1 Introduction

Nanocomposites offer a unique opportunity to exploit the interface phenomena to create new properties and significantly enhance the material responses. [1-5] As described in Chapter 1, in recent years polymer-based nanocomposites were investigated for dielectric applications. [2-15] It was thought that by adding a certain amount of well-dispersed nanoparticles into the polymer matrix, the breakdown field of the polymer would be increased by the interface effect in the nanocomposites, as proposed and discovered by several researchers.[2,6-9] The energy density of the polymer can be improved by increasing the breakdown field. However, the exploration of nanocomposites for dielectric applications is just in its early stage. The effect of nanoparticles on the properties of polymers, especially the electrical and dielectric properties, needs further investigation. It was believed that the polymer-nanoparticle interfaces might play a very important role in determining the properties of nanocomposites due to a large amount of polymer-nanoparticle interfaces in nanocomposites. In comparison with traditional composites with micro-size fillers, large portion of nanocomposites is polymer/nanoparticle interface, whose properties may be quite different from pure polymer and nanoparticles.[8,9,16,17]

In general, the energy density $U_e$ of a diphasic composite can be represented by:

$$U_e = f_1 U_{e}^{(1)} + f_2 U_{e}^{(2)} + g U^{(3)}$$ 5.1
where \( f_1 \) and \( f_2 \) are volume fractions of the constituent dielectric materials in a composite and \( U_e^{(1)} \) and \( U_e^{(2)} \) are their corresponding energy densities, \( U_e^{(3)} \) is the energy density associated with interface effects, and \( g \) is proportional to the interfacial area—either a positive or negative contribution to energy density. For nanocomposites, the contribution from the third term (the interface contribution) can be significant and should be exploited. Eq. 5.1 also indicates that in order to reach high electric energy density, it is preferred that both constituents possess high energy density.

Based on these considerations, in this chapter P(VDF-TrFE-CFE) terpolymer-based nanocomposites were investigated for dielectric materials of high energy density. The terpolymer, ZrO\(_2\) and TiO\(_2\) are all dielectric materials with high energy density. The dielectric constant of ZrO\(_2\) (~20) and TiO\(_2\) (~34 for anatase phase and ~114 for rutile phase) is close to that of the terpolymer matrix (~50) and both oxides have high breakdown electric field comparable to terpolymer.[18-21] It is preferred that the dielectric contrast between the constituents of the nanocomposites is small. This is necessary because in a 0-3 composite, the large dielectric constant contrast will result in a much higher local field in some regions of the composite compared with the average applied field, which will lead to much reduced dielectric breakdown strength of the composite compared with the neat polymer. It will be shown that the nanocomposites with a small amount of nanoparticles exhibit a significantly enhanced polarization response, and consequently a great increase in the electric energy density. The mechanisms of this phenomenon and effect of nanofillers on the dielectric, thermal and electrical properties of the polymer matrix will be discussed in this chapter.

5.2 Experimental

The relaxor ferroelectric P(VDF-TrFE-CFE) (64/36/7.2) mol% terpolymer was chosen as the matrix, which displays a maximum energy density ~9 J/cm\(^3\). ZrO\(_2\) and TiO\(_2\) nanoparticles were purchased from Sigma-Aldrich. The average particle size of ZrO\(_2\) is about 40 nm and that of TiO\(_2\) (anatase phase) is less than 25 nm.
The nanocomposites were prepared using the solution cast method. The terpolymer was dissolved in N, N-Dimethylformamide (DMF, from Sigma-Aldrich) or 2-Butanone (MEK, from Sigma-Aldrich) with suitable concentration. ZrO$_2$ and TiO$_2$ nanoparticles were first dried at 100-120°C in a vacuum oven for 8 hours to remove the absorbed water on the particle surface. After that, the powder was dispersed in DMF solvent and the suspension was stirred using ultrasound to break agglomeration. To further remove agglomeration, the suspension was filtered by a filter with pore size of 0.2 µm. After the above process, the concentration of the nanoparticle suspension was calculated. Finally, the nanoparticle suspension and terpolymer solution were mixed together, stirred by ultrasound, and then poured onto a clean glass slide and dried at 70°C for 5 hrs. Before electrical characterization, the film was annealed for 8 hours (120-130°C) in a vacuum oven to improve the crystallinity and remove residual solvent. It was found that the humidity of the environment in the nanocomposite preparation was critical to produce nanocomposites with well-dispersed ZrO$_2$ nanoparticles. By controlling the humidity in less than 30% during the whole nanocomposite preparation process, we can achieve nanocomposites with well dispersed ZrO$_2$ nanoparticles. The dynamic light scattering technique (Malvern Mastersizer 2000) was employed to monitor the dispersion of the ZrO$_2$ nanoparticles in DMF.

The polymer chain conformation was characterized by Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 510) and the film thickness for the FT-IR test is below 10 µm. X-ray diffraction measurement was carried out using a Scintag Cu K$_\alpha$ diffractometer (x-ray wavelength 1.54 Å). The dispersion of nanoparticles in the terpolymer was checked by Scanning Electron Microscope (SEM, Hitachi S-3000H) and Transmission Electron Microscope (TEM, Philips 420).

The film thickness used for electrical characterization is between 12-20 µm. Sputtered Au electrodes were utilized for the electrical characterizations. A multi-frequency LCR meter (HP4284) was used for the dielectric property measurement. The unipolar and bipolar polarization-electric field (P-E or P-E) loops were measured by a modified Sawyer-Tower circuit and the discharged energy density was calculated from the P-E loops. In addition, the discharged energy density was also acquired by measuring
the discharge energy density of the terpolymer capacitor to a load resistor by using the discharge circuit shown in Chapter 2. It was found that the two measurements yielded the same results. Only the discharged energy density acquired from the modified Sawyer-Tower circuit is presented. The nonlinear dielectric response as a function of applied electric field was characterized using a Sawyer-Tower circuit combined with a function generator (Goldstar FG2002C), a high voltage power supply (Trek, Model 610D), and a lock-in amplifier (Stanford Research Systems).[22] The breakdown field of the nanocomposites was tested by applying a linearly increasing voltage with ramp rate of 500 V/s. The electrode size of the samples for the breakdown test was about 2.5 mm in diameter. For the thermally stimulated current (TSC) measurement, the film sample was first poled at room temperature by applying an electric field of 50 MV/m for 5 min. Then the sample was heated with a ramp rate 2°C/min and the thermally stimulated current was measured by a pA meter.

5.3 Experimental results of P(VDF-TrFE-CFE) terpolymer/ZrO₂ nanocomposites

5.3.1 Characterization of ZrO₂ nanoparticles

Figure 5-1 shows the XRD patterns of as-received ZrO₂ nanoparticles. The sharp diffraction peaks suggest the nanoparticles are in crystalline phase. The ZrO₂ nanoparticles were found to be mainly monoclinic phase mixed with a certain amount of tetragonal phase.[23]

Experimental results have shown that if the nanofillers were not heat-treated at high temperature, the properties, especially the electrical properties, of nanocomposites would deteriorate due to the absorbed water on the surface of the nanoparticles. Nanoparticles, unlike micro-sized particles, possess a much larger surface area/volume ratio. Also, the surface chemistry of particles is quite different from the bulk materials because the crystal lattice ends at the surface and a large amount of broken bonds exist on the surface. Hydroxyl groups resulting from these broken bonds, which can make the
nanoparticles very hydrophilic, were found that on the surface of the nanoparticles.[7] Large amounts of water from the atmosphere would be absorbed on the surface of nanoparticles due to the very large surface area. The absorbed water was found to greatly influence the dispersion of nanoparticles in the solvent and the properties of nanocomposites.

Figure 5-2 shows the DSC results of the nanoparticles. For the first heating run, a very broad peak can be observed just above 100°C, which is thought to be caused by the release of absorbed water. After the powder is heated to 300°C, the absorbed water can be totally removed. For the second heating run, no peak can be observed. As a comparison, for micro-size particle (5-20µm), in the first run, such a peak can hardly be observed, which suggests the different surface properties between micro-size and nano-sized particles. This result also demonstrates the importance of heat treatment of nanoparticles and the control of humidity during the nanocomposite processing. From our experimental observation, nanocomposites prepared by nanoparticles without proper heat treatment or under conditions without humidity control, exhibited poor electrical properties, such as
high dielectric loss and high conductivity, than the composites prepared under proper controlled conditions.

The importance of heat treatment of ZrO₂ nanoparticles before dispersion was further confirmed by the measurement of dielectric properties of the nanoparticles. The nanoparticles were pressed into pellets by applying a high pressure. The dielectric properties were measured after sputtering gold electrode on both sides of the pellet, as shown in Figure 5-3 (in the figure, considering that the nanoparticles could not be compacted to the highest density and the measurement of the dimension of pellets has large error, the dielectric constant vs. frequency curves were divided by a factor to adjust the dielectric constant so that the dielectric constant of all samples at 1 kHz is about 20 (the reported value)). As shown in the figure, the dielectric relaxation at low frequency range, which is related to the absorbed water on the surface, is greatly reduced by heat treatment of the nanoparticles in a vacuum oven above 100°C. From the real part dielectric constant and dielectric loss on the figure, the imaginary dielectric constant ε'' of the nanoparticles can be calculated. The conductivity σ of nanoparticles can then be estimated by:

![Figure 5-2: DSC of ZrO₂ nanoparticles (first run and second run) and micro-sized ZrO₂ particles](image)

The importance of heat treatment of ZrO₂ nanoparticles before dispersion was further confirmed by the measurement of dielectric properties of the nanoparticles. The nanoparticles were pressed into pellets by applying a high pressure. The dielectric properties were measured after sputtering gold electrode on both sides of the pellet, as shown in Figure 5-3 (in the figure, considering that the nanoparticles could not be compacted to the highest density and the measurement of the dimension of pellets has large error, the dielectric constant vs. frequency curves were divided by a factor to adjust the dielectric constant so that the dielectric constant of all samples at 1 kHz is about 20 (the reported value)). As shown in the figure, the dielectric relaxation at low frequency range, which is related to the absorbed water on the surface, is greatly reduced by heat treatment of the nanoparticles in a vacuum oven above 100°C. From the real part dielectric constant and dielectric loss on the figure, the imaginary dielectric constant ε'' of the nanoparticles can be calculated. The conductivity σ of nanoparticles can then be estimated by:
where \( f \) is the measurement frequency. By using \( \varepsilon'' \) under low frequencies, the conductivity of nanoparticles without heat treatment is found on the order of \( 10^{-7} \) S.m\(^{-1}\) and that of nanoparticles after heat treatments is around \( 10^{-8} \) S.m\(^{-1}\), one order smaller than untreated particles.

The ZrO\(_2\) nanoparticles can be well-dispersed in DMF by following the procedures described in the experimental part. As shown in Figure 5-4, the particle size of ZrO\(_2\) in DMF peaks at 40 nm and is overall below 100 nm. Because of the existence of hydroxyl groups on the surface of nanoparticles, it was thought that hydroxyl groups might form hydrogen bonds with oxygen atoms in DMF, which improves the dispersion of ZrO\(_2\) nanoparticle in DMF. It was also found that for composites formed from the solutions with ZrO\(_2\) nanoparticles agglomerated, as detected by the light scattering technique, very little enhancement in the polarization response and energy density, as will be discussed later, were observed, which suggests the importance of particle dispersion on properties of nanocomposites.

Figure 5-3: Weak field dielectric constant of ZrO\(_2\) nanoparticles (measured after pressing the particles into pellets)

The ZrO\(_2\) nanoparticles can be well-dispersed in DMF by following the procedures described in the experimental part. As shown in Figure 5-4, the particle size of ZrO\(_2\) in DMF peaks at 40 nm and is overall below 100 nm. Because of the existence of hydroxyl groups on the surface of nanoparticles, it was thought that hydroxyl groups might form hydrogen bonds with oxygen atoms in DMF, which improves the dispersion of ZrO\(_2\) nanoparticle in DMF. It was also found that for composites formed from the solutions with ZrO\(_2\) nanoparticles agglomerated, as detected by the light scattering technique, very little enhancement in the polarization response and energy density, as will be discussed later, were observed, which suggests the importance of particle dispersion on properties of nanocomposites.
5.3.2 Thermal properties of P(VDF-TrFE-CFE) terpolymer/ZrO$_2$ nanocomposites

As has been observed by many earlier studies, adding nanoparticles in a semicrystalline polymer may alter the crystallization behavior and improve the crystallinity in which the nanoparticles may act as the nucleation agents.[5,24,25] The DSC data of the nanocomposites measured during the cooling scan are presented in Figure 5-5. One immediate effect revealed from the data is that the nanoparticles in the composites raise the crystallization temperature by nearly 10$^\circ$C, from $\sim$ 99$^\circ$C in the terpolymer to $\sim$108.5$^\circ$C in the nanocomposites, which shows indeed the nanoparticles facilitate the crystallization process in the terpolymer matrix. What’s more intriguing is that such an increase in the crystallization temperature occurs with only 0.3 vol% of nanoparticles. Further increase in nanoparticle loading to beyond 0.3 vol% resulted in no further change in the crystallization temperature. On the other hand, no noticeable change in the melting temperature of the terpolymer matrix was observed in the DSC heating scan. The DSC data taken in the heating scans for the nanocomposites are summarized in Table 5-1. In addition to the crystallization temperature, the data indicate that even with 0.3 vol% of the nanoparticles, the crystallinity in the terpolymer matrix (as measured by heat of melting of the melting transition) is increased by about 15% on average. Once
again, for nanocomposites with more than 0.3 vol% of ZrO₂ nanoparticles, no further change in the crystallinity was observed. It should be pointed out that the crystallinity of the terpolymer shown here is a little different from the data reported in the previous chapter, due to different processing and annealing conditions.

Figure 5-5: DSC of the ZrO₂ nanocomposites during the cooling cycle

Table 5-1: The melting temperature Tₘ and heat of melting of nanocomposites

<table>
<thead>
<tr>
<th>Volume percentage of ZrO₂ (vol%)</th>
<th>Heat of melting (J/g)</th>
<th>Tₘ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.46</td>
<td>128.71</td>
</tr>
<tr>
<td>0.3</td>
<td>22.20</td>
<td>127.32</td>
</tr>
<tr>
<td>1</td>
<td>23.24</td>
<td>129.33</td>
</tr>
<tr>
<td>1.6</td>
<td>23.62</td>
<td>128.91</td>
</tr>
<tr>
<td>3.2</td>
<td>23.86</td>
<td>129.89</td>
</tr>
<tr>
<td>6.3</td>
<td>21.92</td>
<td>128.88</td>
</tr>
</tbody>
</table>
Because the glass transition temperature cannot be clearly observed from the DSC data, the DMA of the nanocomposites was measured. The temperature dependence of the loss tangent data under 2 Hz is shown in Figure 5-6. As already discussed in the previous chapters, the relaxation process around -10°C is thought to be associated with the glass transition of the terpolymer, which is exhibited as a shoulder on another much larger relaxation peak. Incorporation of ZrO₂ nanoparticles into the terpolymer was found to suppress the magnitude of this relaxation. One of the reasons may be related to the improvement of crystallinity of the terpolymer by adding nanoparticles. A slight shift of this relaxation process to lower temperature can also be observed on the figure and the shift can be more clearly seen from the inset on Figure 5-6. The decrease of glass transition temperature is also confirmed by the dielectric data, which will be described in detail in the following section.

Figure 5-6: Mechanical loss tangent measured from DMA of the terpolymer and its nanocomposites

The reduction of glass transition of the terpolymers suggests the existence of nanoparticle/polymer interfaces in the nanocomposite. In the polymer/inorganic particles composites, the properties of polymer chains surrounding the particles may be quite
different from their bulk properties. Depending on the affinity between the polymer and particles, the particles may limit (high affinity case, increasing glass transition temperature) or increase (low affinity case, decreasing glass transition temperature) the chain mobility at the interface between polymer and particles. [26,27] This interface region was found to be around 3-9 nm, but considering the gradual change of properties of the polymer chain, the interface may affect a much larger volume of polymer than expected.

Because of very large surface area to volume ratio in nanoparticles, especially for nanoparticles less than 100 nm, the interfacial region in the nanocomposite affect much larger volume than conventional composites with micro-sized fillers. For example, for a nanocomposite with 1.6 vol% 40 nm diameter nanoparticles, assuming spherical shape of the nanoparticles and that the nanoparticles are ideally dispersed (uniformly distributed), it is calculated that one nanoparticle occupies a cubic volume with about 125 nm side length. The distance of polymer between two nanoparticles is estimated to be about 80 nm. If we assume that the influence of the interface region can be as far as 20 nm, about 50 vol% polymer was modified by adding nanoparticles. As a result, in nanocomposites, nanoparticles may greatly affect the properties of polymer, which can be shown as the change of some macroscopic properties. Increase or decrease of glass transition temperature of polymer due to the limitation or increase of chain mobility in interfacial region by adding nanoparticles is one effect of nanoparticle incorporation. Such property change cannot be observed in the conventional composite with micro-sized fillers because of much less interface area.

The reduction of glass transition in P(VDF-TrFE-CFE)/ZrO$_2$ nanocomposites suggests the low affinity between nanoparticle and terpolymer and increase of chain mobility by nanoparticle addition.
5.3.3 Characterization of crystal structure and chain conformations of nanocomposites

X-ray data of (100, 220) diffraction of the nanocomposites with different compositions are presented in Figure 5-7. No marked change in the x-ray peak position was found. The data show that the terpolymer matrix is still in the non-polar phase, which is the same as the terpolymer without nanoparticles.

![XRD patterns of the terpolymer and its ZrO₂ nanocomposites](image)

**Figure 5-7:** XRD patterns of the terpolymer and its ZrO₂ nanocomposites

The FT-IR spectra of nanocomposites are shown in Figure 5-8. No significant change of chain conformations can be observed after the incorporation of nanoparticles. Similar to the pure terpolymer, the chain conformations of nanocomposites are a mixture of TG, T₃G and all-trans (Tₘ>4) conformations. This result is consistent with the XRD result that there is no marked crystal structure change after incorporation of nanoparticles.
5.3.4 Characterization of microstructure of the terpolymer/ZrO$_2$ nanocomposites by SEM and TEM

The morphology of the nanocomposite and dispersion of nanoparticles in the nanocomposites were examined by SEM and TEM. Figure 5-9(a) shows the surface morphology of the nanocomposite (1.6 vol% ZrO$_2$). Only a few large particle agglomerates can be observed. The dispersion of nanoparticles in the nanocomposite was further checked by TEM. As shown in Figure 5-9(b) (the scale on the figure is 100 nm), in the nanocomposite samples, the nanoparticles are well-dispersed. The dark spots in the figure are corresponding to ZrO$_2$ nanoparticles. The size of the nanoparticles is around 40nm, which is consistent to the particle size measured by the light scattering technique. In some samples, large agglomerates larger than 100 nm can also be observed, as shown in Figure 5-9(c). The composition of the dark spots was identified as ZrO$_2$ by EDS.

Figure 5-8: FT-IR spectra of the terpolymer and its ZrO$_2$ nanocomposites
5.3.5 Weak field dielectric properties of the terpolymer/ZrO₂ nanocomposites

Temperature dependence of the weak-field dielectric properties of pure terpolymer, nanocomposite with highest volume percentage of ZrO₂ nanoparticles (6.3 vol%) in this study, and nanocomposite with intermediate ZrO₂ content (1.6 vol%), is presented in Figure 5-10. The weak field dielectric properties of the nanocomposites do not show much change compared with the terpolymer matrix. However, if we take a close look at this data, it can be found that incorporation of nanoparticles into the terpolymer matrix indeed modifies the dielectric properties of the polymer matrix.
Figure 5-10: Weak field dielectric properties of (a) neat terpolymer (b) nanocomposites with 1.6 vol% nanoparticles and (c) nanocomposites with 6.3 vol% nanoparticles as a function of temperature at different frequencies (dielectric constant (from top to bottom), and dielectric loss (from bottom to top): 0.1k, 1k, 10k, 100k, and 1 MHz).
Figure 5-11(a) shows the dielectric loss (1 kHz) of the pure terpolymer and nanocomposites with various compositions in the temperature range between -20°C and 10°C. In this temperature range, the dielectric loss peak, which is related to the glass transition of the terpolymer, can be observed to shift slightly to lower temperature with an increasing amount of nanoparticles, from about -3.18°C for the pure terpolymer to about -6.92°C for the nanocomposite with 6.3 vol% ZrO₂. This experimental result is consistent with the DMA result that incorporation of nanoparticles will reduce the glass transition temperature of the polymer matrix. It should also be noticed that the dielectric loss is first decreased with increasing nanoparticle content up to 1 vol% then increased in this temperature range. The nanocomposite with 6.3 vol% ZrO₂ exhibits highest dielectric loss, indicating other possible polarization mechanisms contributing to the dielectric properties of nanocomposites, especially in the composites with high particle loading.

For the real part dielectric constant, on the contrary, it was found that the dielectric maxima shifted to a higher temperature with increasing amount of ZrO₂ nanofillers, as presented in Figure 5-11 (b), which shows the temperature dependence of dielectric constant of terpolymer and its nanocomposites at 1 kHz. The dielectric maxima shift to higher temperature for about 2°C when the loading of the nanoparticles changes from 0 to 6.3 vol%. Although the terpolymer is a relaxor ferroelectric material and it does not possess a specific Curie temperature, the temperature at which the dielectric maxima occur can be considered as an indication of phase transition temperature between polar and nonpolar phases. Shift of dielectric maxima to higher temperature suggests that incorporation of ZrO₂ nanoparticles may stabilize the polar phase in the terpolymer.

Similar to the dielectric loss shown in Figure 5-11 (a), the dielectric constant of nanocomposites in the temperature range around the dielectric maxima tends to first decrease with increasing amount of ZrO₂ and then increase when the volume percentage of the nanoparticles is higher than 1.6 vol%. The largest dielectric constant was found in the composite with 6.3 vol% nanofillers. It’s normal that the dielectric constant of nanocomposites is lower than pure terpolymer because the dielectric constant ZrO₂ (~20) is much lower than terpolymer (higher than 50), but it is anomalous that the dielectric constant was increased by adding nanoparticles with low dielectric constant. This result
Figure 5-11: The temperature dependence of (a) dielectric loss at 1 kHz (b) dielectric constant at 1 kHz (c) dielectric constant at 1 MHz of the terpolymer and the nanocomposites
further suggests that other polarization mechanisms may contribute to the dielectric response of the nanocomposites.

When the measurement frequency was increased to 1MHz, the dielectric constant of the nanocomposite with 6.3 vol% ZrO₂ was greatly reduced to a value lower than pure terpolymer, as shown in the Figure 5-11(c). It means the polarization mechanism, which contributes to the dielectric response of nanocomposites with high percentage of ZrO₂, is a frequency-dependent process.

5.3.6 Unipolar loops and energy density of terpolymer/ZrO₂ nanocomposites

In contrast to weak field dielectric properties, the nanocomposites exhibit a quite different polarization response at high electric fields. Figure 5-12 shows the unipolar P-E loops for nanocomposites with various volume percentages of ZrO₂ nanoparticles (the unipolar P-E loops of terpolymer can refer to Figure 2-5). Compared with the unipolar P-E loops of pure terpolymer shown in Chapter 2, under the same electric field, nanocomposites generate higher induced polarization. For example, for the nanocomposite with 1.6 vol% of ZrO₂, even under 300MV/m electric field, polarization can reach more than 0.11 C/m², while under the same field, the neat terpolymer displays a polarization of about 0.07 C/m². For the neat terpolymer, the saturation polarization never exceeds 0.1 C/m². Consequently, the nanocomposites exhibit higher energy density under the same electric field, compared with pure terpolymer, as summarized in Figure 5-13(a), where even with 0.3 vol% of ZrO₂ nanoparticles has resulted in an increase in the energy density by more than 35%. For composites with 1.6 vol% nanoparticles, the energy density is 10.5 J/cm³ under 300 MV/m, which represents about 45% increase compared with the neat terpolymer (~ 7.3 J/cm³). This energy density is even higher than the energy density of the neat terpolymer at near the polarization saturation (9 J/cm³ under 400 MV/m). For nanocomposites with more than 1.6 vol% nanoparticles, no further increase in the energy density is observed, indicating the saturation effect with more addition of nanoparticles.
Figure 5-12: The unipolar P-E loops of the nanocomposites with (a) 0.3 vol\% (b) 1 vol\% (c) 1.6 vol\% (d) 2.3 vol\% (e) 3.2 vol\% and (f) 6.3 vol\% ZrO$_2$ nanoparticles
From the unipolar P-E loops, the discharge efficiency of the nanocomposites can be deduced, as shown in Figure 5-13(b). The discharge efficiency decreases when the loading of the nanoparticles is higher than 3.2 vol%.

The saturation effect can also be observed from the unipolar P-E loops. Figure 5-14(a) summarizes the unipolar P-E loops of nanocomposites of various compositions under the electric field of 250 MV/m and Figure 5-14(b) presents the composition dependence of maximum induced polarization and “remnant” polarization from the Figure 5-14(a). We can see that the maximum polarization first increases with volume fraction of ZrO$_2$, reaches a maximum value at the nanocomposite with 2.3 vol% ZrO$_2$ and then decreases. The “remnant” polarization, which may be caused by the conduction loss or some slow relaxation process, as discussed in Chapter 2, is continuously increased when the volume fraction of ZrO$_2$ is higher than 1.6 vol%. This result suggests the maximum enhancement of polarization occurs at the composition of between 1.6 and 3.2 vol%. Further addition of ZrO$_2$ nanoparticles above this optimum value also leads to higher remnant polarization and higher conduction loss. Therefore, considering the energy density and energy loss of the nanocomposites, the optimum volume percentage of ZrO$_2$ particles is in the range between 1.6 and 3.2 vol%. Too much ZrO$_2$ particle
loading can not improve the energy density and the energy loss can be also significantly increased at the same time.

Figure 5-14: (a) Comparison of unipolar P-E loops of nanocomposites with various compositions under an applied field of 250 MV/m and (b) variation of the maximum polarization and the “remnant” polarization with volume percentage of ZrO₂ under 250 MV/m
5.3.7 TSC of nanocomposites

Figure 5-15 shows the comparison of TSC curves between the pure terpolymer and the nanocomposite with 1.6 vol% nanoparticle. Under the same poling conditions, the nanocomposite generates one or two orders higher thermally stimulated current than the pure terpolymer, which originates from the trapped space charge in the samples. This experimental result is different from the previous report that the existence of nanoparticles could mitigate the space charge accumulation in the polymer.[8] For nanoparticles, because periodical crystal structure ends at the surface, there are a large number of broken bonds on the particle surface. The imperfect surface may provide a large quantity of charge trap sites. Also taking account of very large surface to volume ratio, it is reasonable that a large amount of charges were trapped around the polymer/particle interface regions when an electric field was applied on it. [28] The controversy between our and previously reported results may arise from the different affinity between polymer and nanoparticles.[8] In their cases, the polymer and nanoparticle pair might possess good affinity and the polymer could be covered on the surface of the nanoparticles, by which the trap sites were reduced. [8] The TSC result further confirms that the affinity between the terpolymer and ZrO₂ may be poor.

5.3.8 Breakdown field of the terpolymer/ZrO₂ nanocomposites

The comparison of the breakdown fields between the terpolymer and the nanocomposite with 1.6 vol% ZrO₂ is presented in Figure 5-16. The terpolymer and nanocomposite samples for the breakdown test were prepared under the same conditions. Incorporation of nanoparticles into terpolymer slightly reduces the breakdown field from ~306 MV/m (this breakdown field is different from the proceeding chapters because they are from different batches) to ~292 MV/m. At the same time, the shape parameter β is reduced from 4.6 to 3.7. The reduction of breakdown field may also be the result of the poor affinity between terpolymer and ZrO₂ nanoparticles, which leads to the space charge accumulation, as shown in the TSC result. The accumulation of space charge deforms the
Figure 5-15: Thermally stimulated current of the terpolymer and the nanocomposite with 1.6 vol% ZrO₂

Figure 5-16: Weibull analysis of breakdown field of the terpolymer and the nanocomposite with 1.6 vol% ZrO₂
electric field distribution in the nanocomposite and generates large field concentration near the nanoparticle and polymer interface, which results in early electric breakdown.[8] Addition of nanoparticles can also increase free volume and generate new voids in the polymer and these factors can reduce the breakdown field of the nanocomposites.

5.4 Discussions about the terpolymer/ZrO₂ nanocomposites

5.4.1 Effect of nanoparticle on the crystal structure of the terpolymers

Previous research found that incorporation of nanoparticles into the PVDF polymer could result in β phase, instead of α phase.[29-31] In our case, XRD and FT-IR were employed to detect the possible structural change in the nanocomposites, but no obvious structural change was found by these methods. However, the possibility of minor change of structure can not be excluded. XRD reflects the overall change of structure and it might not be accurate enough to detect the slight structural change in the interface regions. For FT-IR data, many factors, such as baseline subtraction, peak overlap and peak fitting, also make it difficult to find the possible structural change. However, the shift of the glass transition temperature observed by DMA and the temperature dependence of dielectric loss has already verified the existence of an interface region that may have different crystal structure from the bulk polymer.

From the dielectric data shown in Figure 5-11, a slight shift of dielectric maxima to higher temperature with an increasing amount of nanoparticles is observed. As already mentioned, the temperature at which dielectric maxima occur can be seen as an indication of phase transition temperature between the polar and nonpolar phases. Shift of the temperature to higher temperature means the polar phase is stabilized by the nanoparticles. Therefore, under the same temperature, nanocomposites probably possess higher ratio of polar to nonpolar phases than terpolymer, but the difference may not be very significant, which can not be detected by XRD or FT-IR.
5.4.2 Mechanisms for the improvement of energy density in the nanocomposites

It is interesting to observe that addition of a small amount of ZrO$_2$ nanoparticles into PVDF terpolymer can greatly enhance the polarization response and the energy density of the polymer. Because the dielectric constant of ZrO$_2$ is much lower than the terpolymer, this phenomenon contradicts the mixing rule of composite materials. Several mechanisms may contribute to the enhancement effect of nanocomposites.

The crystallinity change is first considered to be one reason for the enhancement effect because for semicrystalline polymers, their dielectric response comes mainly from the crystalline phase. DSC results have shown that the crystallinity of terpolymer was improved by adding nanoparticles. However, the increased crystallinity should not be the major cause for the observed increase in the energy density in the nanocomposites since (i) the increased crystallinity of the terpolymer matrix due to the presence of nanoparticles becomes saturated above 0.3 vol% of nanoparticle content while the increase in the energy density with nanoparticles continues till 1.6 vol% of nanoparticles. (ii) The crystallinity increase due to the presence of nanoparticles is about 15% while increase in the energy density is more than 40%. (iii) The nanocomposites exhibit higher polarization level (>0.11 C/m$^2$) even under an applied field of 300 MV/m. This polarization level is about 50% higher than terpolymer under the same electric field.

Based on the experimental results and the above discussions, it is proposed that the large amount of polymer/nanoparticle interfaces play a more important role for this phenomenon. DMA and dielectric data show that addition of nanoparticles improves the chain mobility of the polymer at the polymer/nanoparticle interface which will reduce the energy barrier for polarization switching. In terpolymer, the polarization switching process is mainly the transformation from non-polar phase to polar phase. Addition of nanoparticles also tends to favor the polar molecular conformation against the non-polar phase in the polymer. As a result, a lower field is required in nanocomposites to induce the conformation change from the non-polar phase to polar-phase compared with the terpolymer matrix. All the above factors can enhance the polarization response of nanocomposite.
The reduction of energy barrier for polarization switching and transformation between nonpolar and polar conformations was confirmed by measurement of the effective dielectric constant (the ratio of P/E) as a function of applied field of the neat terpolymer and nanocomposite with 1.6 vol% ZrO₂ at room temperature, as shown in Figure 5-17. At low fields, the dielectric constant of the terpolymer matrix is higher than that of the nanocomposite due to the lower dielectric properties of ZrO₂ nanoparticles. The effective dielectric constant of the nanocomposite increases faster than that of the terpolymer matrix due to the lower energy barrier for polarization switching in nanocomposite. At an electric field higher than 35 MV/m, the effective dielectric constant of the nanocomposite surpasses that of the terpolymer matrix.

![Figure 5-17: The effective dielectric constant as a function of the applied electric field of the terpolymer and the nanocomposites. At above 35 MV/m, the nanocomposite exhibits higher effective dielectric constant.](image)

Stabilization of polar phase in nanocomposite is supported by the comparison of the bipolar P-E loops between nanocomposite and pure terpolymer. Figure 5-18 shows bipolar P-E loops of nanocomposite and terpolymer at zero degree. Under the same field nanocomposite possesses a fatter polarization hysteresis loops, which is more close to
normal ferroelectric materials, and higher polarization response than the terpolymer because the polar phase possesses higher dipole density than nonpolar phase.

In addition to the contribution from the increase of crystallinity and polymer/nanoparticle interface, one third possible mechanism for the enhancement is a certain kind of frequency dependent interfacial dielectric response, especially for nanocomposites with high loading of the nanoparticles, as observed from weak field dielectric data. It is expected that this polarization mechanism may also contribute to high field polarization response. It is still not clear whether this additional contribution is from space charge polarization or the Gouy-Chapman-Stern double layer, proposed by several authors. [16,17,32].

The polarization and energy density saturation effect of the nanocomposites may also be a result of the existence of the polymer/nanoparticle interfaces. As mentioned above, in the nanocomposite with 1.6 vol% ZrO$_2$ nanoparticles, about 50% of polymer matrix is affected by nanoparticles. When the volume percentage of ZrO$_2$ is increased to about 3.2 vol%, complete overlapping of the interfacial region can be expected. It is interesting to observe that the saturation effect also occurs in this composition range. This

![Bipolar P-E loops of the terpolymer and the nanocomposite with 1.6 vol% ZrO$_2$ nanoparticles.](image)

Figure 5-18: Bipolar P-E loops of the terpolymer and the nanocomposite with 1.6 vol% ZrO$_2$ nanoparticles.
indicates that the coalescing and overlapping of the interface regions, as schematically shown in Figure 5-19, may deteriorate the dielectric properties of the nanocomposites.

Figure 5-19: Schematic illustrating the interface effect and possible cause for the saturation of the interface effects due to the coalescing of the interface regions as the nanoparticle volume fraction increases.

It has been proposed that the interfacial region in the nanocomposite be more conductive than the bulk polymer materials. [8] Our experimental results from the unipolar P-E loops show an increase of loss, partially from conduction loss, with increasing amount of nanoparticles, which supports this hypothesis.

5.4.3 Dielectric nonlinearity of nanocomposites

In Chapters 2 and 3, we showed that for a dielectric polymer such as the relaxor ferroelectric terpolymer, a lower dielectric constant (lower than 50 for the weak field dielectric constant which is that for the terpolymer matrix) is preferred in order to delay the polarization saturation so that a higher energy density can be achieved. On the other hand, by raising the polarization, a higher energy density can also be obtained. In other words, for the nanocomposites here, it is not the reduction of the weak field dielectric constant of the polymer that delays the polarization saturation and leads to higher electric energy density. Instead, it is the enhanced polarization achieved in the terpolymer matrix that “delays” the polarization saturation and results in a higher electric energy density. As seen from Figure 5-12, the nanocomposites exhibit a much higher polarization ($P_{\text{max}} \sim 0.11 \text{ C/m}^2$ under 300 MV/m) compared with that in the terpolymer matrix ($P_{\text{max}} \sim 0.085$
C/cm² under 400 MV/m). As a quantitative comparison, effective dielectric constant $\varepsilon_{\text{eff}}$, defined as $U_e=\frac{1}{2} \varepsilon_{\text{eff}} \varepsilon_0 E^2$ where $\varepsilon_0$ is the vacuum permittivity, was calculated. As shown in Figure 5-20, for the pure terpolymer, owing to the “early” polarization saturation, $\varepsilon_{\text{eff}}$ decreases with field rapidly and at 300 MV/m, the terpolymer has a $\varepsilon_{\text{eff}} \sim 15$. The higher polarization in the nanocomposites leads to a delay in the polarization saturation. At 300 MV/m, the nanocomposites with 1.6 vol% of nanoparticles show a $\varepsilon_{\text{eff}} \sim 26$, much higher than that in the terpolymer. Consequently, the nanocomposites exhibit a much enhanced electric energy density.

![Chart](image)

**Figure 5-20**: The energy density and effective dielectric constant vs. applied field for (a) the terpolymer and (b) the nanocomposite with 1.6 vol% ZrO₂ nanoparticles

**5.5 Polarization and energy density enhancement effect in terpolymer/TiO₂ nanocomposites**

The terpolymer/TiO₂ nanocomposites were also investigated and compared with the results of the terpolymer/ZrO₂ nanocomposites. A similar phenomenon of polarization and energy density enhancement was observed in the terpolymer/TiO₂ nanocomposites (the unipolar P-E loops of pure terpolymer can be found in Chapter 2), although the effect is less significant than terpolymer/ZrO₂ nanocomposites, as shown in
Figure 5-21 (a), (b) and (c), the unipolar P-E loops of the nanocomposites with various volume fractions of TiO$_2$ nanoparticles, and Figure 5-21(d), the calculated discharged energy density. Analogous to the terpolymer/ZrO$_2$ nanocomposites, the saturation of energy density can also be observed from Figure 5-21(d), but the saturation effect occurs at a lower volume fraction in TiO$_2$ nanocomposites than the ZrO$_2$ nanocomposites, probably due to the smaller particle size of TiO$_2$ (less than 25 nm) than ZrO$_2$ nanoparticles (around 40 nm).

Figure 5-21: Unipolar P-E loops of nanocomposites with (a) 0.5 vol% (b) 1.5 vol% (c) 5 vol% TiO$_2$ nanoparticles and (d) the energy density of the terpolymer/TiO$_2$ nanocomposites
5.6 Summary

In this chapter, the dielectric properties and microstructure of the P(VDF-TrFE-CFE) terpolymer/ZrO\textsubscript{2} and terpolymer/TiO\textsubscript{2} nanocomposites were investigated by various characterization techniques. The enhancement of the high field polarization response and the energy density was observed in these two nanocomposite systems. The enhancement effect was mainly from the polymer/nanoparticle interfacial regions, the existence of which was verified by the experimental results of DMA and the temperature dependence of dielectric loss. The shift of glass temperature to a lower temperature of the nanocomposites with an increasing amount of the nanofillers indicates the poor affinity between nanoparticles and polymer matrix. The chain mobility of the polymer matrix in the interface regions is improved by adding nanoparticles. At the same time, incorporation of nanoparticles also favors the polar phase in terpolymer. As a result, the energy barrier between the polar and nonpolar phases is reduced. Also, for the terpolymers, because their dielectric responses reach maxima around room temperature, the dielectric response is very sensitive to the structure change and this energy barrier change. All these factors lead to a higher polarization response and energy density of the nanocomposites than the pure terpolymer under the same electric field. Other effects, including the improvement of crystallinity by adding nanoparticles and an additional interfacial dielectric response, especially for the composites with high volume fraction of nanoparticles, also contribute to the enhancement effect.

Experimental results show that overlapping of the interfacial regions will deteriorate the high field dielectric response. The polarization response and energy density of the nanocomposites exhibit the saturation effect with increasing amount of nanoparticle loading. The optimum particle loading depends on the size of nanoparticles. For the terpolymer/ZrO\textsubscript{2} nanocomposites, the optimum composition is in the range between 1.6 and 3.2 vol\% ZrO\textsubscript{2} nanoparticles.

In the terpolymer/ZrO\textsubscript{2} nanocomposites, a large space charge accumulation and the reduction of breakdown field were found, probably due to the poor affinity between the nanoparticle and polymer matrix.
References


Chapter 6
Conclusions and Future Work

6.1 Conclusions

Two strategies were employed to develop PVDF-based polymeric materials with high dielectric energy density for capacitors applications. The first is to develop new dielectric materials with a reasonably high dielectric constant and high breakdown strength; the second is to investigate multi-component material systems based on the rationale that the interface in multi-component materials may have a beneficial effect on energy density. These strategies were found be effective to improve the energy density of PVDF-based polymers. In this study, P(VDF-TrFE-CFE) terpolymers, P(VDF-CTFE) copolymers, P(VDF-HFP) copolymers, P(VDF-TrFE-CFE) terpolymer/ZrO$_2$ nanocomposites, P(VDF-TrFE-CFE) terpolymer/TiO$_2$ nanocomposites, P(VDF-TrFE-CFE) terpolymer/P(VDF-CTFE) copolymer blends, and P(VDF-TrFE-CFE) terpolymer/PMMA blends were investigated.

6.1.1 P(VDF-TrFE-CFE) terpolymers

CFE acts as defects in the crystalline phase of terpolymers, which break up the polarization coherence and stabilize the non-polar phase. By the defect modification, the terpolymers become relaxor ferroelectric. At room temperature, the terpolymers show a high dielectric constant (>50 at 1 kHz). The terpolymers also exhibit a high breakdown electric field. Intrinsically, the breakdown field of terpolymers can be higher than 400MV/m. A maximum energy density about 10 J/cm$^3$ can be obtained in the terpolymers, which is much higher than that of un-modified P(VDF-TrFE) copolymers and other dielectric polymers for capacitor applications.
Two methods were used to characterize the energy density of the terpolymer. One method is to calculate the energy density from unipolar P (or D)-E loops, and the other method is to measure the energy density by directly discharging the stored energy to a load resistor. The energy density measured by the two methods was found to be fairly consistent with each other. The discharge time of the terpolymers is not in proportional to the load resistor, indicating that ESR is also a determinant factor of discharge time. Change of ESR with discharge speed reflects the frequency dependent and field dependent nonlinear dielectric response of P(VDF-TrFE-CFE) terpolymers.

Two loss mechanisms, conduction loss and dielectric loss, during the charging-discharging cycle were identified from the unipolar P-E loops. The conduction loss is electrode-dependent. The conduction of the terpolymer is mainly controlled by the charge injection from the metal electrode to the polymer, and charge carriers for conduction are mainly hole or electron.

The breakdown field of the terpolymer is dependent on the metal-polymer interface, which suggests that the charge injection from the electrode to the polymer plays an important role in the breakdown process.

### 6.1.2 P(VDF-CTFE) and P(VDF-HFP) copolymers

Although P(VDF-TrFE-CFE) terpolymers possess very high energy density, due to their high dielectric constant they exhibit a highly nonlinear dielectric response and polarization saturation well below the breakdown field. Therefore, the energy density of the PVDF-based polymers can be further improved by developing materials with a suitable dielectric constant to avoid early polarization saturation.

P(VDF-CTFE) (10, 15 and 20 wt% CTFE) and P(VDF-HFP) (10 and 12 wt% HFP) copolymers with a dielectric constant around 12 were investigated. Due to a lower dielectric constant than that of the terpolymer, the early polarization saturation is avoided and a high energy density (larger than 24 J/cm³) was obtained in these copolymers.

Similar to P(VDF-TrFE-CFE) terpolymers, from thermal, dielectric and microstructure characterizations, it was found that bulky HFP and CTFE were
incorporated into the crystalline phase as defects. Due to the defect modification, the crystallinity of copolymers is greatly reduced by incorporation of CTFE and HFP, which reduces the maximum polarization response of the copolymer. However, also due to the defect modification, the nonpolar phase is stabilized and the ferroelectric domain size is reduced, resulting in the destruction of polarization coherence of ferroelectric domains. The remnant polarization is therefore reduced, which increases the discharge energy density. As a result, high energy density can be obtained in the copolymers due to the reversible transition between the nonpolar and polar phases. In addition to the defect-modified crystalline phase, the crystalline-amorphous interphase may also contribute to the high energy density of these copolymers.

The discharge time of the P(VDF-CTFE) (15 wt% CTFE) copolymer was found to depend mainly on the load resistor, indicating the low ESR of the materials.

6.1.3 P(VDF-TrFE-CFE)/P(VDF-CTFE) and P(VDF-TrFE-CFE)/PMMA blends

Based on the solubility parameter calculation, it was thought that the P(VDF-TrFE-CFE) terpolymers might not be completely miscible with P(VDF-CTFE) copolymers. For P(VDF-TrFE-CFE)/P(VDF-CTFE) blends, experimental results from the dielectric data, DSC, DMA, SEM confirmed that the terpolymer and the copolymer could be partially miscible. Enhancement of polarization response and energy density in the blends with the 5 wt% and the 10 wt% P(VDF-CTFE) copolymer was observed. One possible reason for the enhancement is the increase of crystallinity and possible structural change. Based on the experimental results and past research reports, the enhancement phenomenon may also be related to the interface effect of the blends. The breakdown field of the blends is improved by about 100 MV/m due to the improvement of storage modulus by adding a small amount of the copolymer. The energy density of the blends, which is about 11.5 J/cm³ (the maximum value), is greatly improved compared with the pure terpolymers.

The P(VDF-TrFE-CFE) terpolymers and PMMA can be miscible with each other. PMMA can greatly reduce the crystallinity and weak field dielectric constant of the
blends. Due to the improvement of the storage modulus, the breakdown field of the blends can be improved. The optimum composition of the blend is about 2.5 wt%. For this composition, the breakdown field can be improved without reduction of the polarization response.

6.1.4 P(VDF-TrFE-CFE) terpolymer/ZrO$_2$ and P(VDF-TrFE-CFE)/TiO$_2$ nanocomposites

Significant enhancement of the polarization response and energy density were observed in the terpolymer/ZrO$_2$ and terpolymer/TiO$_2$ nanocomposites with a small amount of ZrO$_2$ or TiO$_2$ nanoparticles (less than 6.3 vol%). For terpolymer/ZrO$_2$ nanocomposites (1.6 vol%), a polarization response of about 0.11 C/m$^2$ and an energy density of about 10.5 J/cm$^3$ can be achieved in a much reduced electric field (300 MV/m). For the terpolymer, under the same electric field, the polarization is only around 0.07 C/m$^2$ and energy density is 7.3 J/cm$^3$. For the neat terpolymer, the maximum polarization response is not higher than 0.1 C/m$^2$ and the maximum energy density for this composition is 9 J/cm$^3$. The enhancement is caused by the large volume percentage of the polymer/nanoparticle interface in the nanocomposite.

From the DMA and dielectric data, the reduction of the glass transition temperature of nanocomposites was observed, which is caused by the increase of chain mobility around the polymer/nanocomposite interface. Increase of the transition temperature between the nonpolar and polar phases was also observed, indicating that addition of nanoparticles may favor the polar phase. The effect of nanoparticles is to reduce the energy barrier between the polar phase and nonpolar phase in the terpolymers, resulting in the enhancement of the polarization response and energy density.

Nanoparticles can also significantly improve the crystallinity of the terpolymer, which is another reason for the polarization and energy density enhancement. An interfacial polarization, which was found in the nanocomposites with a high volume percentage of nanoparticles, may also contribute to the enhancement.
The optimum loading of nanoparticles is between 1.6 vol% and 3.2 vol% for ZrO$_2$ nanoparticles. Due to the overlapping of interface regions, higher loading may result in lower polarization response and higher conduction loss. For TiO$_2$ nanoparticles, due to the smaller particle size, the optimum loading shifts to a lower volume percentage.

Experimental results showed that the interaction between the nanoparticle and the terpolymer was weak, which resulted in a lower glass transition, lower breakdown field and larger space charge accumulation in the nanocomposites.

### 6.2 Future work

The exploration of dielectric materials with high energy density will be continued in order to approach the energy density limit of nature. As shown in this study, two strategies can be utilized to improve energy density.

Although P(VDF-CTFE) and P(VDF-HFP) copolymers have shown very high energy density, because of their low dielectric constants, even under the highest applied electric field, they still do not show signs of polarization saturation. Therefore, new polymers with a dielectric constant between that of terpolymers and copolymers can be designed. It is possible that higher energy density can be obtained in the PVDF-based polymers under a reduced electric field.

Multi-component material system is another way to improve energy density. This study has shown that the interfaces of polymer/polymer and polymer/nanoparticle may contribute to the energy density of composite materials. However, the interfaces of the multi-component system are still not well understood. Many questions, such as how the interfaces are related to the properties of the components, how the interfacial properties change with the fillers’ size, and how the two components interact with each other, need to be answered. Through further study and understanding, the contribution from the interface to energy density can be exploited to improve the energy density of the dielectric materials by design, either by improvement of the breakdown field or enhancement of polarization response, or both.
In addition to the interfaces in the composite materials, another interface phenomenon, the interface between the metal electrode and the polymer, needs further study. As shown by the experimental results of the terpolymer, the polymer/metal interface plays a very important role in the conduction and breakdown of terpolymers. Further work is needed to understand the interface between the metal and the polymer to improve the breakdown field and reduce the conduction loss of the terpolymer.

For the materials that have been developed, further work is required to improve the performance of these materials. For example, the performance of the terpolymer and the copolymer can be further improved by cross-linking. Cross-linking can reduce energy loss, which can improve the reliability under a high electric field. Cross-linking can also improve the temperature stability and mechanical properties of these polymer materials to extend the applications of these materials in the higher temperature range.
VITA

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Baojin Chu was born on July 1st, 1975, in Yantai, Shandong Province, China. He received his Bachelor degree in Ceramic Engineering from Shandong Institute of Light Industry in 1997. He got his Master degree in Materials Science and Engineering from Shanghai Institute of Ceramics, Chinese Academy of Sciences in 2000. He continued his research in the same institute for two years and then worked as visiting researcher in Korea Institute of Ceramic Engineering and Technology until 2003. In August 2003, He was admitted to the Graduate School of the Pennsylvania State University. His thesis work was concentrated on PVDF-based polymers for capacitor applications.