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EFFECT OF TENSILE STRAIN ON THE MORPHOLOGY AND DIELECTRIC PROPERTY OF PVDF BASED COPOLYMERS

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ABSTRACT

Electro-active polymers have great impact on many current technologies such as sensors and actuators, energy storage and flat panel display. An important families of electro-active polymer: polyvinylidene fluoride (PVDF) based polymer, are studied in this thesis to investigate the effect of mechanical stretching on its microstructure and dielectric properties.

In comparison with other linear dielectric polymers, PVDF-based polymers have a much higher polarization responses under an external applied electric field. The maximum polarization level of PVDF-based polymer can be high as 0.1 C/m$^2$. And an estimated energy density of 30J/cm$^3$ is expected in this class of polymers\cite{1}\cite{2}. This is greater than energy density achieved by PVDF homopolymers and copolymers because of the polarization hysteresis in these polymers. PVDF and its copolymers with ferroelectric nature are often chosen because of they can admit an efficient electrical to mechanical actuation in response to external electrical stimulation. The optimization of these properties is related to the degree of crystallinity, structure, and orientation of the crystalline part of polymer. These parameters are heavily depending on the processing conditions.

When cooling from melt, PVDF based copolymers commonly crystallize in the non-polar crystalline $\alpha$-phase. However, the electroactive properties depend on polar $\beta$-phase and its structural characteristics. The $\beta$-phase can be induced by several methods, the one investigated in this study being the mechanical stretching of the $\alpha$-phase at suitable temperature\cite{1}\cite{2}. The $\alpha$ to $\beta$ phase transformation of PVDF-BTFE copolymer through the stretching process at different temperatures was investigated. The optimum stretching conditions were studied and characterized by infrared spectroscopy, WAXD and differential scanning calorimetry. The maximum $\beta$ phase content was achieved at 110 C with a stretch ratio of 5. An orientation of the polymer chains with specific packing preferences in crystalline structure is observed in the experiment. FTIR spectroscopy was used to examine the structural variation as function
of strain. DSC data allowed the measurement of melting temperatures and enthalpies of material before and after stretching. Energy and intensity variation was also investigated at different deformations. Reorientation of the chain from perpendicular to parallel to stress direction was observed. The lamellae thickness does not change significantly during stretching.
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Chapter 1

Introduction

Polymers are important class of material for the life of human beings, including daily product such as plastic packaging material to advanced electronic devices such as OLEDS. Polymers have replaced many traditional functional materials such as metals and ceramics due to their light-weight and low cost advantage [1][3][4]. Compared to the passive polymer materials, high energy electro-active polymers have brought the attention in recent decades because of their desirable functionalities in many important fields. The emerging electro-active polymers have shown big impact on a broad range of applications such as fiber-optics, fuel cells, high energy density capacitors, flat panel display, sensor and actuators.

In order to meet the high challenges and demands of advanced technologies, variety of high performance polymers are studied. The main focus is on using proper processing method to achieve better electrical properties. This thesis focuses on development and characterization of uniaxial stretched PVDF based copolymer for two types of applications: dielectric and piezoelectric applications.
Chapter 2

Literature Survey and Statement of Work

PVDF based materials has long been used as life time coatings, chemically inert materials and electrical insulator. The large piezoelectric effect of PVDF has been discovered in 1969, with the piezoelectric coefficient of poled thin films as large as 6-7 pC/N, which is about 10 times greater than other polymers. Extensive study has carried out to investigate the ferroelectric and piezoelectric nature of PVDF by exploring its structure-property relationship \(^{[2]}\). Many PVDF based devices was introduced, such as actuators, transducers and pyro-electric devices. In the last decades, ferroelectric behavior has been discovered in defect modified PVDF based copolymer and terpolymer. The modification results in significant increase of dielectric constant as well as electromechanical strength in PVDF.

PVDF has a glass transition temperature (Tg) of -35 °C and is usually 50-60% crystalline. The polymer chains are packed into different crystalline forms (phases) in the crystalline region\(^{[2]}\). There are four major crystalline phases: α, β, γ and δ phases, which depend on the way of packing and conformation of each individual chain. The α phase and β phase are the most important phases for ferroelectric applications\(^{[2]}\).

Synthesis of PVDF

PVDF is commonly produced by free radical polymerization of 1,1-difluoethylene at elevated temperature (50-150 °C) and high pressure (10-300 atm). The most common process used is emulsion and suspension process using water as reaction medium. Inorganic persulfate or organic peroxide can be used as catalyst. Since the PVDF monomer have directionality (head to head or head to tail), usually 5% of monomer units is incorporated in reverse direction. This can cause the 8% reduction in dipoles.
Structure-property relationship for PVDF based copolymers

-Effect of Crystal structure and Crystal Orientation

In α phase, the chain conformations are represented as a sequence of alternating trans and gauche sequences (TGTG, trans-gauche-trans-gauche) shown in Figure 1. The α phase forms in the monoclinic unit cell with space group P2₁/C (a=4.96A, b=9.64A, c=4.62 A, β=90°). In this structure, each unit cell has two VDF repeat unit. The adjacent chains are packed in a way that the dipole moments of the individual C-F bonds are aligned perpendicular to chain direction, which cancels each other out. The directions of chain are built from an average up-up and up-down orientations\(^\text{[1]}\).

![Figure 1-1: Schematic view of α phase crystal, with a=4.96 A, b= 9.64A, c=4.62A](image)

In β phases, two chains in planer TTTT (all trans) zigzag conformation are packed into individual orthorhombic unit cells (with space group Cm2m, a=8.58 A, b=4.9A, chain direction c=2.56A). It can be noted that in all-trans conformation, the fluorine atoms are positioned on the same side of the unit cell, resulting in a net dipole moment. In fact, the β phase is very polar, having a net dipole moment of 2.1 Debye \(^\text{[1]}\). When the structure of unit cell of β phase crystal satisfies the symmetric requirement of a piezoelectric crystal, this form of PVDF will responsible for its piezoelectric properties.

![Figure 1-1: Schematic view of β phase crystal, with a=8.58 A, b=4.91A](image)
In \( \gamma \) phase, the chain conformation is approximately TTTG-TTTG’, with space group C2cm. When the high electric field is applied to the \( \alpha \) phase, it will cause 180 rotation of alternate chains leading to a polar monoclinic \( \delta \) phase crystal \(^{[2]}\). Different phases exist in PVDF-based polymer is highly processing dependent. Different synthesis conditions like melt temperature, solvent, annealing condition and method of casting/stretching of thin films will result in different crystalline phase.

The first principle calculation results show that \( \alpha \) phase is the most stable phase (Su et al. 2004). In most cases, PVDF forms \( \alpha \) phase when prepared cooling from melt or solution cast. Mechanical stretching is often used to obtain ferroelectric \( \beta \) phase from \( \alpha \) phase. In some cases, the \( \beta \) phase can form directly for \( P(VDF-TrFE) \) copolymers with VDF content less than 80% \(^{[5]}\). In the semicrystalline polymer, these crystallites are oriented randomly in the polymer. This random chain configuration contributes to the absence of piezoelectric activity. In order to generate piezoelectric properties within polymer, the domains must be oriented in strong electric field (poling field). Poling is usually achieved by electroding the polymer surface with metal electrode, and applying strong electric field.

The \( \beta \) phase can also be obtained by spin coating PVDF/DMF solution with addition of \( Mg(NO_3)_2*6H_2O \) and dried at 100 °C \(^{[5]}\). For the stretching method mentioned earlier, the deformation of \( \alpha \) phase (non-polar) results in transformation to \( \beta \) phase (polar) only happens when stretching below certain temperature. For \( PVDF-BTFE \) copolymer, this temperature happened to be 110 °C. B. Mohammadi et al. has shown the effect of stretch rate on conversion of \( \alpha \) phase to \( \beta \) phase \(^{[6,7]}\). Maximum \( \beta \) phase content was obtained at 90°C during stretching \(^{[8]}\).
The γ phase can be produced by either casting from DMSO or dimethylformamide solution regardless of preparation temperature \[9\]. It can also produce by crystallizing from melt under high pressures. The conversion of γ phase to β phase is still unclear from literature studies.

The origin of large polarization in PVDF and its copolymers is the strong dipole moment perpendicular to the polymer chains. In β-phase crystals, the crystals possess net dipoles in their unit cells. As a result, their polarizability is remarkably high when under an external electric field, which lead to high dielectric constant. In the α-phase, the neighboring dipole moments are in the opposite directions, thus the crystal unit cell exhibits zero net dipoles \[^1\]. The polarizability of PVDF crystals is highly depending on orientation of dipole moment under low frequencies. Alignment of dipole moments with applied electric field is through crank-shaft or chain flipping motions.

**Figure 1-3. Schematic diagram of crystalline orientation before and after stretched**

*-Effect of Polymorphism and Crystallite Size*

The lamellae thickness of typical PVDF crystalline regions is around 10 to 20 nm. The polymer chains are folded between upper and lower lamella surfaces with chain stems between folds oriented preferentially normal to the lamellae plane \[^4\]. As shown in Figure 3, the lamellae further form spherulites. The crystalline chain fold regions are surrounded by amorphous chains. The crystalline phase of PVDF is
highly dependent on processing method. For example, $\alpha$ phase forms from melt solidification. And it can be transformed into $\beta$ phase by unaxially stretching. When $\alpha$ phase is subjected to high electric fields, it will be converted to $\delta$ phase then to $\beta$ phase at extreme fields \[^{[4]}\]. Thus, $\beta$ phase is the most attractive phase for applications of PVDF for its piezoelectric effects.

![Schematic view of crystal morphology of polymer](image)

**Figure 1-4.** Schematic view of crystal morphology of polymer

The PVDF based polymers have outstanding electrical properties due to their relatively easy phase transformation between the paraelectric $\alpha$ phase and ferroelectric phases ($\beta$, $\delta$, $\gamma$ phases), which enhances the ferroelectricity under strong electric field \[^{[4]}\]. However, the dielectric loss ($\tan\delta$) for $\alpha$ and $\beta$ crystal phases, which due to relaxation of electric dipoles, are nearly 0.02 at 1 kHz under room temperature \[^{[5]}\]. It is much higher than the current commercialized dielectric capacitor films. For example, biaxial oriented polypropylene only has dielectric loss of 0.0002 at 1 kHz. Relaxation of polarization of the ferroelectric phase at relatively low electric field decreases the energy density of the material \[^{[4]}\]. Thus, the relatively high loss, early polarization saturation and large ferroelectricity hindered the application of PVDF as advanced high energy density film capacitors.
Experimental data suggested that coupling behaviors among ferroelectric domains can be adjusted by different polymorphism and crystallite size [4]. This, in turn, determined dipole reorientation and switching behaviors. High $\beta$ phase content and large grain size enabled the coupling behaviors among ferroelectric domains. As a result, dipoles in highly coupled domains can be polarized in a relative easy manner which contributes to the high energy density and dielectric constant of the material. However, high remnant polarization as a result of coupling interaction significantly reduces the discharged energy density. After reduction of grain size, the coupling interaction among ferroelectric domains has been significantly weakened. Therefore, PVDF copolymer film with high $\beta$ content and small grain size will enable high energy density storage.

In order to reduce the cooperative ferroelectricity in the PVDF crystals, different was of chemical structure modification has been investigated in recent years. For instance, certain amounts of bulky co-monomers such as bromotrifluoroethylene (BTFE), chlorotrifluoroethylene (CTFE) or hexafluoropropylene (HFP) were randomly introduced in the PVDF main chain to reduce grain size. The resulting P(VDF-BTFE) or P(VDF-HFP) copolymers thus exhibited the relaxor ferroelectricity and able to maintain a energy density of 18-25 J/cm$^3$ [4]. The high energy density was a result of the broadened and reversible $\alpha$ to $\beta$ phase transformation. Polystyrene (PS), as a low loss polymer mentioned previously, was grafted onto P(VDF-BTFE) chains in order to reduce the dielectric loss of the copolymer. Upon crystallization, the PS formed a layer trapping around the PVDF crystallites, which reduces the compensation polarization happened at the crystalline/amorphous interface of PVDF copolymers. As a result, a low loss and higher energy density can be achieved by grafting PS on the main chain [4]. All this findings could greatly assist us to achieve ideal crystalline morphology in PVDF copolymers for high energy storage applications.
- *Effect of Molecular Weight and Temperature*

In general, the electrical breakdown strength increases with increasing molecular weight and decreasing temperature. This is due to the qualitative degree of crystallinity of polymers decreases as molecular weight increases. Increasing molecular weight impede some of the crystallization process through the creation of inter and intra chain entanglement. These crystalline properties were favorable to isolate the molecular weight impact from any potential effects that large crystallinity difference might have.

As molecular weight increases, the yield stresses of the polymer increases. This makes the films more resistant to Maxwell electrostatic compressive forces between electrodes and thus lead to high breakdown strength\(^5\).

Decreases temperature will also lead to the increase in yield stresses. This increase in yield stress originates from the stiffening of chains as polymer approaches and passes its glass transition temperature. As lower temperatures, the free volume of polymer decreases which increase the force required to slide each polymer chain passing each other\(^5\). As a result, the dielectric breakdown strength increases with decreasing temperature. Another thermal breakdown mechanism might take places in this case. Thermal breakdown occurs when the electrical power dissipate heat to reach some critical breakdown temperature which leads to the melting or degradation of polymer. Thermal heating could soften the polymer and causes electromechanical failures at low field.

The conductivity decreases as molecular weight increases. This is a result of decrease of crystalline content. Electromechanical breakdown due to Maxwell stress is identified as primary reason of electric failure at room temperature\(^5\). Thermal breakdown contributes to Maxwell breakdown process at temperature near or below glass transition temperature.
Copolymer/ Terpolymer composition can also affect the dielectric permittivity of polymer. For example, P(VDF-TrFE-CTFE) terpolymer can have significant variation in dielectric strength by modifying its TrFE and CTFE compositions. According to the experiment by Jason Claude [8], DSC study indicates an increase of the melting temperature of polymer with decreasing CTFE content. The T3GT3G’ in the γ-phase and TGTG’ conformation in the α phases are converted to the all-trans conformation of β phase when more TrFE is introduced into the polymer. The elongated trans sequences increase the activation energy for dipole alignment which limits polarization responses. On the other hand, due to the formation of smaller g- crystals with T3GT3G’ conformation that respond readily to the electric field, the polymer exhibit the highest dielectric permittivity in this case [8].

CTFE in the terpolymer coverts the normal ferroelectric into relaxor ferroelectric. This creates variety of ferroelectric nanoscopic domains. When applying electric field, the T3GT3G’ conformation transforms to polar ferroelectric domains with all-trans conformations [8]. The positive dependence of breakdown strength on crystallinity and modulus suggests that the electromechanical breakdown mechanism is mainly responsible for electrical failure in these polymers.

**Phase Transitions**

The energy barrier for PVDF phase transformation is considerably high. It has been long studied that ferroelectric phase of PVDF can be altered by introducing certain defects into its structure. For example, by introducing TrFE into the PVDF, it developed all trans chain conformation due to the existence of extra fluorine atoms which impede polymer chain from forming the trans-gauche (TGTG) conformation. As a result, polymer will able to form β phases while crystallizing at room temperatures [11]. Yu et al. showed that electron irradiation can produce structural defects into β phases, which stabilize the
nonpolar phase at room temperature. Similar effect can be achieved by introducing small amount of termonomer (ie. CFE, CTFE or HFP) as crystal defect. The defect induced by CTFE units randomize the inter and intra-chain polar coupling.

Figure 1-5: Phase diagram of P(VDF-TrFE) polymers showing a ferroelectric to paraelectric transition \[^{[1]}\]

Figure 1-5 marks the ferroelectric polar phase (FE) to paraelectric (PE) nonpolar phase transition. The FE to PE transition temperature increases with increasing VDF content. When the temperature is below Tc, the crystal is in an ordered all-trans structure. As temperature rises and passes the PE-FE transition, more gauche bonds are formed within the all-trans structure. This resulted in a disordered crystalline state, which lead to the formation of PE phases containing mixed TG and TTTG \[^{[1]}\]. As temperature continues increasing, the polymer will passes through the melt transition. As noticed in Figure 1-4, there is no apparent FE-PE transition under high VDF content. It appears that the melting takes place before the transition. It is because under high VDF content, the conformational defects is introduced as temperature rises, making it difficult to form paraelectric nonpolar phase.
PVDF based composite material

As mentioned earlier, most polymer-based materials have relatively low dielectric constant ~4. Another approach to improve the dielectric constant of polymer is to introduce another component with high dielectric constant, normally ceramic particles. However, the inclusion of micro-sized particles will also reduce the breakdown field and discharged energy density. In order to solve this problem, nano-sized particles was adding into the polymer which not only will improve the dielectric constant, but also improve the breakdown field due to the interface effect in nanocomposite.

A direct method to improve dielectric constant is by addition of high dielectric constant materials. In general, PbTiO₃, BaTiO₃ and (PMT-PT) possess very large dielectric constant. For example, by introducing PMN-PT nanoparticles into P(VDF-TrFE) copolymer will increase its dielectric constant to 250. The breakdown field is also high, 130MV/m. Since the significant effect of interface between polymer and nanoparticles on the dielectric properties, it is very crucial to study the nature of nanocomposite interface [20][21].

Another method to improve the dielectric constant is by adding semi-conductive fillers in the insulating matrix. As a result, the dielectric constant is greatly improved at a threshold volume. In this case, the dielectric constant can be increased to tens or hundreds times. For instance, the Cu-Pc/PANI/PU system has dielectric constant of 800 [8]. Many people focusing on polymer/metal composites these years.

A serious problem for this type of material is the increase of dielectric loss with dielectric constant. When the amount of composites reaches the percolation threshold, the dielectric loss become very high and will greatly reduce the breakdown field. Fortunately, people have solved this problem by coating the metal particles with a layer of carbon cell which reduces the dielectric loss of the nanocomposites.

Carbon nanotube (CNT)/PVDF nanocomposites have been extensively studied in recent years since CNT shows large shape anisotropy, high mechanical strength and very high electrical conductivities [9]. CNT is superior choices for nanocomposites because of its nanometer-scale dimension. PVDF and its copolymers are often chosen as host polymer because they allow an efficient electrical to mechanical
energy conversion and be able to create large actuation in response to applied electric field. The CNT/PVDF nanocomposites would satisfy the need because their dielectric constant is high when the CNT concentration is near the percolation threshold. However, the dielectric properties of CNT/PVDF system would often change due to the microstructure shift when the composites are stretched under a relative high strain. In general, dielectric constant and conductivity would decrease after stretching the composites \[9\]. This is due to rearrangement of multiwall carbon nanotubes along the tensile strain direction.

**Improvement of breakdown field in nanocomposites**

The PVDF nanocomposite has superior mechanical properties due to a large ratio of surface to particle volume and huge interfacial areas between nano-fillers and polymer matrix. Nano-filler can improve the dielectric properties of polymer based on the large amount of interfacial interactions. By putting in less than 10wt% of nano-fillers can significantly increase the breakdown field, alleviate the internal space charge accumulation which lead to high energy density and high field performance.

**Dielectric properties of PVDF based copolymers (CTFE, HFP, etc)**

![Figure 1-6. Structure of P(VDF-HFP) copolymer](image)

For PVDF based polymers, the induced polarization will reach maximum value under high applied electric field. With the polarization saturation, large non-linear dielectric fluctuation can be observed. If the polarization saturation is far below breakdown field, the dielectric material will not reach
Defect modified P(VDF-CTFE) and P(VDF-HFP) both have a dielectric constant around 14 (at 1kHz, room temperature) which is stronger than other polymeric materials for capacitor applications. These two polymers have good electromechanical properties and possess high energy density of 25 J/cm³. By arranging the composition of VDF/TrFE to be 70/30, the polymer will have a near zero remnant polarization with large polarization change[9]. The relaxor like behavior was obtained by the lowering of energy barrier between polar and non-polar conformations [9]. The bulkier size of CTFE and HFP comonomer expand the VDF inter-chain space and distort the crystalline ordering. As a result, the copolymer results in large dielectric constant and lower dipole density than PVDF homopolymer. By modification, the conformation energy of TGTG’ is lowered and a reversible conformation change between α phase and β phase is achievable. This will lead to large polarization change without early saturation. Also the polarization will saturate at high electric field which enables high energy density applications.

**Dielectric relaxation process**

The dielectric constant of these two copolymers does not vary much from room temperature to 100 °C. This is attractive for dielectric applications. As shown in Figure 1-7, two loss peaks appear in the temperature range. The first peak was due to glass transition (dynamic Tg). The first peak also might due to the relaxation process in the crystalline/amorphous interface[22]. The dielectric maximum takes place at 110 °C for PVDF homopolymer. Corresponding to the maximum, a loss peak at 80 °C is observed. This second dielectric maximum might be related to the defects in crystalline phase[21][22]. As the CTFE
content increases, the dielectric maximum is lowered and shifted to a lower temperature. Also the magnitude of loss peak is greatly reduced as CTFE content increases. This indicates that introducing CTFE modifies crystalline phase of PVDF and reduces the degree of crystallinity.

Figure 1-7. (a) Dielectric constant and (b) Dielectric loss at 1kHz of PVDF homopolymer and P(VDF-CTFE) copolymer with different composition\textsuperscript{[22]}
Dielectric Properties of P(VDF-TrFE-CFE) Terpolymer

Based on previous study, P(VDF-TrFE-CFE) terpolymer can possess very high dielectric constant (~50) at room temperature. The high dielectric constant and thin polarization hysteresis suggest that PVDF-based terpolymers are able to achieve high energy density.

Due to the steric hindrance effect of TrFE, all-trans conformation is adapted. In fact, all-trans form is the most polar phase in PVDF-based polymer. After CFE is introduced, the bulky CFE breaks the ferroelectric ordering. By introducing 8mol% CFE into P(VDF-TrFE), the polar conformation almost disappears and corresponding non-polar TG conformation increases\textsuperscript{[21][22]}.\footnote{\textsuperscript{[21][22]}}

Energy loss is another important concern for terpolymer for capacitor applications. The energy loss converted into heat and increases the temperature of polymer. The dielectric loss impedes the application of polymer film under high electric field and reduces the dielectric breakdown. The energy loss mainly due to conduction\textsuperscript{[21][22]}. When the applied electric field is returned to zero, the polarization response deviate and does not return to zero. The polarization deviation is mainly due to conduction process.
Statement of Work

The goal of the work is to explore the effect of mechanical stretching on the electrical properties of PVDF based copolymers. For this final goal, the compositions-structure-property relationship of PVDF-based polymer, nanocomposites were investigated in this work. The work can be divided into the following categories:

1. P(VDF-BTFE) copolymers with various BTFE content have been developed in our group, which shows a high dielectric constant and excellent electromechanical properties. The relationship between dielectric constant, breakdown field and energy density will be studied in this work.

2. Effect of hot stretching on P(VDF-BTFE) copolymers will be studied. Our investigation is an attempt to provide exhaustive data on dielectric relaxation behavior of hot pressed and uniaxial stretched PVDF-BTFE films.

3. The literature review will focus on the structure-property relationships of PVDF-based copolymer. Effect of crystalline orientation, polymorphism, crystallite size, molecular weight and copolymer composition on the electrical property of PVDF based polymer will be extensively investigated.
Chapter 3

Experimental Procedure

Materials

All solvent and reagents in this study were purchased from VWR and used as received. Ethyl hydroxyl cellulose (EHEC) was used as received from Polymer Lab Inc. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under Argon protection. Vinlylidene fluoride and bromotrifluoroethylene were purchased from SynQuest Laboratory Inc. The monomers were purified by freeze thaw process before use.

Synthesis

PVDF-BTFE copolymer was synthesized by suspension polymerization using hydrogen peroxide as initiator. Ethyl hydroxyethyl cellulose (EHEC) was used as surfactant. 300ml stainless steel Parr reaction vessel is used for the polymerization process. Suspension polymerization reaction performed first by adding 100 mL deionized water as the reaction medium and 0.2 g ammonium peroxodisulfate as initiator. The reactor was degassed by repeated freeze thaw cycles and cooled by liquid nitrogen. Prescribed amount of VDF and BTFE were added to the reactor at liquid nitrogen temperature. Once the reagents are cooled, gaseous vinlylidene fluoride (VDF) was added at constant flow rate and varying times followed by vacuuming to original level. Gaseous bromotrifluoroethylene (BTFE) was added then at constant flow over varied times followed by another vacuuming of the vessel. The vessel was then disconnected from the monomer flow line and sealed then heated to 90° C, stirred at 600 rpm, and allowed to react for 24 hours. Resulting polymer is filtered and washed with methanol/water for 3 times and final product were dried to constant weight in vacuum. The powder form P(VDF-BTFE) with various wt% BTFE were synthesized by varying the gaseous BTFE flow time. The polymer films for the
electrical test were prepared by compression molding at 200 °C for 30 min. The film prepared by compression molding was found to exhibit better quality and higher breakdown field than solution cast method. The films were quenched to room temperature after compression molding. For some measurements, the film was stretched uniaxially to about 5 times its original length by the zone drawing method in the temperature range between 100 °C and 110 °C.

Table 1-1. Flow rates information for different samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>VDF Flow Rate (cm³/min)</th>
<th>BTFE Flow Rate (cm³/min)</th>
<th>VDF Flow Time (min)</th>
<th>BTFE Flow Time (s)</th>
<th>Moles VDF</th>
<th>Moles BTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>523.6</td>
<td>385</td>
<td>17.5</td>
<td>0</td>
<td>.378</td>
<td>0</td>
</tr>
<tr>
<td>1.1</td>
<td>523.6</td>
<td>385</td>
<td>21</td>
<td>7</td>
<td>.454</td>
<td>.002</td>
</tr>
<tr>
<td>1.25</td>
<td>523.6</td>
<td>385</td>
<td>17.5</td>
<td>10</td>
<td>.378</td>
<td>.003</td>
</tr>
<tr>
<td>1.5</td>
<td>523.6</td>
<td>385</td>
<td>17.5</td>
<td>25</td>
<td>.378</td>
<td>.007</td>
</tr>
<tr>
<td>2</td>
<td>523.6</td>
<td>385</td>
<td>17.5</td>
<td>45</td>
<td>.378</td>
<td>.012</td>
</tr>
<tr>
<td>3</td>
<td>523.6</td>
<td>385</td>
<td>17.5</td>
<td>90</td>
<td>.378</td>
<td>.024</td>
</tr>
<tr>
<td>4</td>
<td>523.6</td>
<td>385</td>
<td>17.5</td>
<td>120</td>
<td>.378</td>
<td>.032</td>
</tr>
<tr>
<td>5</td>
<td>523.6</td>
<td>385</td>
<td>17.5</td>
<td>157</td>
<td>.378</td>
<td>.042</td>
</tr>
</tbody>
</table>

Characterization

¹H NMR spectra were conducted on Bruker AM-300 spectrometer. NMR measurements were carried out by dissolving 90g of each sample in THF and performed on a Bruker CDPX-300 NMR for 200 scans. The thermal properties of film sample were obtained by TA Instruments Q100 differential scanning calorimeter (DSC) at heating rate of 10°C/min. Wide angle X-ray diffraction (WAXD) measurements were carried out using Scintag diffractometer with Cu-Ka radiation. FTIR spectra were recorded on Varian Digilab FTS-800 spectrometer from room temperature to 135°C. The dielectric constants of polymer film were obtained using Agilent LCR meter. Gel permeation chromatograph (GPC) was performed using DMF as mobile phase with Viscotek TDA 302 triple detector system.
Chapter 4

Results and Discussions

Synthesis of P(VDF-BTFE)s

\[
\begin{align*}
\text{CH}_2=\text{CF}_2 + \text{CFBr}=\text{CF}_2 & \xrightarrow{\text{BPO, 80}^\circ\text{C}} \left[\left(\text{CF}_2-\text{CH}_2\right)_x \left[\text{CF}_2-\text{CFBr}\right]_y\right] \\
& \Rightarrow \text{P(VDF-BTFE)}
\end{align*}
\]

Figure 2-1. Synthesis of P(VDF-BTFE) copolymers

The synthetic strategy outlined in figure 1 involves the copolymerization of VDF and BTFE using BPO as initiator to yield P(VDF-BTFE) copolymer. For suspension polymerization, high molecular weight copolymers were obtained because of heterogeneous condition and the slow termination step. VDF and BTFE have quite different reactivity ratios in free radical polymerization. (i.e. \(r(\text{VDF})=0.43, r(\text{BTFE})=1.46\)) \cite{25}. It follows that \(r_1/r_2=0.63\). Consequently, the degree of alternation in the equimolar copolymer is less than in case of the corresponding VDF-CTFE system. The chemical compositions of the P(VDF-BTFE) copolymers can still be easily controlled by varying BTFE flow time. In general, for perfluorovinyl monomers M with general formula \(\text{CF}_2=\text{CF-R}\), if R is electron-donating group (CTFE, BTFE), \(1/r(\text{VDF})\) is greater than 1 indicating a higher reactivity of monomer M. A library of 8 P(VDF-BTFE) with different chemical compositions has been prepared.
The compositions of the polymers are determined by $^{19}$F NMR. Figure 3-1 shows the $^{19}$F NMR spectrum of P(VDF-BTFE) copolymer with composition of VDF/BTFE = 80/20 mol%, and the peak assignments are shown below.

Different signals of each monomeric unit were observed. Peak at -91 ppm corresponds to the difluoromethylene group in $-$CH$_2$CF$_2$-CH$_2$CF$_2$-CH$_2$CF$_2$-, the peaks at -94.8, -113.4 and -115.7 ppm correspond to $-$CH$_2$CF$_2$-CF$_2$CH$_2$-CH$_2$CF$_2$-CH$_2$-CF$_2$- and CH$_2$CF$_2$-CF$_2$CH$_2$-CH$_2$CF$_2$- respectively. These three peaks arise from the inversion of VDF base unit in polymer chain; sometime refer to head-to-head or tail-to-tail addition. The peaks from -105 to -108 ppm zone are assigned to difluoromethyl group and to the tertiary fluorine atom in the BTFE microblocks, respectively. The peak at -118 ppm is assigned to the tertiary fluorine atom in BTFE adjacent to VDF unit.

Peak at -40 ppm corresponds to $-$CF$_3$ or $-$CF$_2$Br groups resulting from chain transfer reactions brought on by BTFE. This is the reason why the signal grows with increasing BTFE monomer feed ratio. Peak between -80 and -140 ppm correspond to chain conformation (ie. Head to tail linkages, etc)\[11\]. The copolymer equation of P(VDF-CTFE) can be used in this case due to the similarity between Cl and Br.
Figure 3-1. $^{19}$F NMR spectra of PVDF-BTFE (Sample 5) with VDF/BTFE of 80/20 mol%

Figure 3-2. $^{19}$F NMR spectra of PVDF-BTFE (Sample 1)
Figure 3-3. $^{19}$F NMR spectra of PVDF-BTFE (Sample 1.5)

Figure 3-4. $^{19}$F NMR spectra of PVDF-BTFE (Sample 2)
Figure 3-5. $^{19}$F NMR spectra of PVDF-BTFE (Sample 3)

Figure 3-6. $^{19}$F NMR spectra of PVDF-BTFE (Sample 4)
The chemical composition of P(VDF-BTFE) are calculated according to integrals of characteristic peaks of VDF and BTFE in $^{19}$F NMR spectra by following equation:

$$\frac{X}{1-X} = \frac{S_1 + S_2 + 3S_3 - S_4 \cdot 3}{S_5 + S_6 + 2(S_4 - S_3) \cdot 2}$$

where $S_1$ is the integral intensity of resonance area from 91 to 98 ppm, $S_2 = 105$-108 ppm; $S_3 = 113.4$ ppm, $S_5 = 116$-119 ppm; $S_6 = 120$-124 ppm; $X$ represent VDF mol% while $1-X$ represents BTFE mol%.

The molar ratio of each copolymer sample can be calculated and result is shown below:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mole % VDF</th>
<th>Mole % BTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>1.25</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>90.1</td>
<td>9.9</td>
</tr>
<tr>
<td>2</td>
<td>89.5</td>
<td>10.5</td>
</tr>
<tr>
<td>3</td>
<td>85.9</td>
<td>14.1</td>
</tr>
<tr>
<td>4</td>
<td>85.9</td>
<td>14.1</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

**Differential Scanning Calorimeter**

DSC is the most widely used thermal analysis technique. In this technique, polymer sample and reference material of known heat capacity are heated in separate cells. Samples are heated or cooled at constant rate, usually 10 °C per minutes $^{[12]}$. The instrument measures the heat required to maintain the same temperature in the polymer sample as the reference material. Heat flow is then plotted as function of temperature. Thermal transitions are identified in the curve.
Figure 4-1. Typical thermal graph for semi-crystalline polymer

For melting transition, the enthalpy associated with transition is obtained from the area under the curve for the heat flow versus temperature over the transition.

Figure 4-2. DSC thermogram for sample 1
Figure 4-3. DSC thermogram for sample 1.25

Figure 4-4. DSC thermogram for sample 1.5
Figure 4-5. DSC thermogram for sample 2

Figure 4-6. DSC thermogram for sample 3
The degree of crystallinity was measured as the ratio between $\Delta H_m$ and $\Delta H_0$, where $\Delta H_m$ is the melting enthalpy of the material under study and $\Delta H_0$ is the melting enthalpy of totally crystalline material ($\Delta H_0 = 104.50$ J/g for PVDF).

### Table 3-1. Melting point and degree of crystallinity for PVDF-BTFE samples with different copolymer compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tm</th>
<th>% X-stal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>168</td>
<td>39.95</td>
</tr>
<tr>
<td>1.1</td>
<td>162</td>
<td>36.68</td>
</tr>
<tr>
<td>1.25</td>
<td>159</td>
<td>33.57</td>
</tr>
<tr>
<td>1.5</td>
<td>156</td>
<td>31.89</td>
</tr>
<tr>
<td>2</td>
<td>143</td>
<td>26.82</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>9.4</td>
</tr>
<tr>
<td>5</td>
<td>74</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### Figure 4-7. Melting point and percent crystalline for PVDF-BTFE samples
From the DSC results sample 1.1 composition is determined as in the above plot with indicated a composition of about 5-6 mole % BTFE.

For P(VDF-BTFE) copolymers (Sample 1), two melting peaks, one at about 156°C and the other at about 167°C, can be observed. Both melting peaks move to lower temperature as BTFE content increase. For sample 3, the two melting peaks are at 100°C and 121°C, respectively. From a theoretical standpoint, incorporation of the bulky monomer in the VDF reduces the melting temperature. These copolymer possess highly heterogeneous composition distribution. The reaction rate of BTFE is larger than VDF, which leads to large amount of BTFE in the amorphous phase. Experimental results showed that P(VDF-BTFE) with 20mol% CTFE would be an amorphous polymer (2.5% crystalline). The change of melting temperature of copolymer is a result of the high heterogeneity.

The two melting temperature of the copolymers come from two different types of crystalline phases. One is almost pure PVDF phase and the other is BTFE modified PVDF phase whose peak position shifts to lower temperature with increasing CTFE content. The heat of fusion decreases exponentially with BTFE content. The result shows that BTFE greatly reduces the crystallinity due to structural due to structural irregularity.

Presence of BTFE in PVDF also reduces the crystallization temperature. The crystallization temperature for sample 1 (10 mole % BTFE) is about 145°C and that of sample 3 (14 mole % of BTFE) gives crystalline temperature at about 110°C.

**DSC results for stretched films**

The values of crystalline content of each sample were determined by TA Q1000 DSC, using a heating rate of 10 °C /min. The films were unaxially stretched to a draw ratio of 5. The temperature of
drawing process was held constant at 110°C. Table 3-2 shows the percent crystallinity for sample 1.1 and sample 1.25 stretched at 110 °C with draw ratio of 5. The degree of crystallinity is defined as the ratio between $\Delta H_m$ and $\Delta H_0$, where $\Delta H_m$ is the melting enthalpy of the material under study and $\Delta H_0$ is the melting enthalpy of totally crystalline material.[22]

<table>
<thead>
<tr>
<th>sample</th>
<th>Tm (C)</th>
<th>% X-stal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 unstretched</td>
<td>162.00</td>
<td>36.7</td>
</tr>
<tr>
<td>1.1 stretched</td>
<td>161.42</td>
<td>37.9</td>
</tr>
<tr>
<td>1.25 unstretched</td>
<td>159.00</td>
<td>33.57</td>
</tr>
<tr>
<td>1.25 stretched</td>
<td>157.91</td>
<td>33.58</td>
</tr>
</tbody>
</table>

The unstretched PVDF-BTFE (sample 1.1) film shows endothermic peak at 162°C. This peak is associated with melting of polymer have an enthalpy change of 37.9 J/g. The sharp melting suggests the semi-crystalline nature of polymer. At same time the DSC thermogram of uniaxially stretched film shows melting peak at 161.42 °C. This peak is slightly sharper than the unstretched one and shifted to lower temperature side. With $\Delta H_0 = 103.40$ J/g[17], unstretched PVDF-BTFE (sample 1.1) shows 36.7% crystallinity while upon uniaxial stretching this crystallinity has been increased to 37.9%. This clearly indicates that the deformation process leads to partial construction of the crystalline structure.

The melting temperature was found to be decreased slightly after stretching. It is known that the melting temperature of PVDF semi-crystalline polymers is related with the lamellae thickness. The results shown in Table 3-2 suggest that the strong changes in the morphology during the film drawing contribute to slight decrease in lamellae thickness. As expected, after drawing the polymer chains get more oriented and more packed. DSC results shows that $\Delta H$ is not strongly affected by the stretching ratio.
Gel Permeation Chromatography (GPC) Analysis

GPC was used to find the molecular weights of the polymers of different co-monomer ratios. GPC is an important process in the analysis of polymeric materials. It can determine molecular weight and distribution which is the basis for most properties of polymers.

GPC operates by dissolving a polymer in a solvent and running through a system of rigid highly porous particles. The rate at which the particle flow through the system is depends on particle sizes. The process is depicted below; showing that the small particles are caught as larger ones continues to travel. This allows the separation and collection of particles by size.

Figure 5-1. Schematic diagram of different size of molecule flow through GPC column[18]

Figure 5-2. Basic component of GPC measurements[18]
GPC results for sample 3, 4 and 5 were not ascertained due to weak Refractive Index (RI) response. The results for other samples were listed below:

Table 4-1. GPC results for different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74077</td>
<td>142394</td>
<td>1.922</td>
</tr>
<tr>
<td>1.1</td>
<td>67032</td>
<td>124501</td>
<td>1.857</td>
</tr>
<tr>
<td>1.25</td>
<td>63758</td>
<td>118861</td>
<td>1.864</td>
</tr>
<tr>
<td>1.5</td>
<td>58996</td>
<td>114241</td>
<td>1.936</td>
</tr>
<tr>
<td>2</td>
<td>37787</td>
<td>56012</td>
<td>1.482</td>
</tr>
</tbody>
</table>

The decrease in molecular weight with increase BTFE composition can be attributed to the BTFE chain transfer reaction shown in the $^{19}$F-NMR results.

The reactivity ratio gives understanding on the behavior of each monomer is the copolymerization. If $r>1$ for a given monomer, it means that the monomer is preferred to add its own species. If $r<1$, it means that monomer is preferred to add the other monomer involved in this reaction. If both $r_1 * r_2$ are close to zero, indicating that alternating polymerization is favored. In the common case of $0<r_1 r_2<1$, both $r_1$ and $r_2$ are less than 1. Examining reactivity ratios is a useful way to determine how a given monomer will react in the polymerization. In this case, VDF and BTFE have quite different reactivity ratios in free radical polymerization. (i.e. $r$(VDF)=$0.43$, $r$(BTFE)=$1.46$). It follows that $r_1 r_2=0.63$. Consequently, the degree of alternation in the equimolar copolymer is less than the VDF-CTFE system. As the BTFE content increases, the chain transfer reaction started taking place due to the high reactivity factor of BTFE. This is limiting factor in obtaining high molecular weight polymer.

**Film Stretching**

The 50-um thick P(VDF-BTFE) films were formed by melt-pressing the powder at 230°C followed by immediate quenching in water. A mini stretching unit was used for the stretching studies.
The stretching mechanism has two grips, the bottom one is fixed and the top one is movable. The sample of desired dimension is fixed between the two grips and stretching mechanism is connected to the stepper motor. The 13-mm wide films were fixed (distance between clamps 10mm) and pulled apart at a constant speed of 2mm/min. The rate of movement of top grip in upward direction can be controlled by speed of motor. The stretching is kept inside an oven which can be heated up to 200°C.

Film drawing was performed by heating the film to the desired temperature (110°C). The draw ratio was calculated by the relative length extension of inked lines, 10 mm apart, imprinted on the film before drawing. Samples with different deformations in the range from 400% to 500% were prepared and studied. The thickness after drawing (ratio of 5) was close to 30um.

Table 4-2. Draw ratio and thickness information for the unstretched and stretched P(VDF-BTFE)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Starting Thickness (µm)</th>
<th>Ending Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 (1)</td>
<td>4.4</td>
<td>52</td>
<td>28</td>
</tr>
<tr>
<td>1.1 (2)</td>
<td>5.2</td>
<td>48</td>
<td>19</td>
</tr>
<tr>
<td>1.1 (3)</td>
<td>5.1</td>
<td>55</td>
<td>21</td>
</tr>
<tr>
<td>1.25 (1)</td>
<td>4.7</td>
<td>58</td>
<td>27</td>
</tr>
<tr>
<td>1.25 (2)</td>
<td>4.6</td>
<td>49</td>
<td>23</td>
</tr>
<tr>
<td>1.25 (3)</td>
<td>4.9</td>
<td>50</td>
<td>22</td>
</tr>
</tbody>
</table>

From the standardized stretching experiment, the PVDF deformation can be divided into four parts: crystal rotation, lamellar separation, plastic deformation and breaking. As shown in Figure 6-1. During the tensile drawing experiment, the PVDF-BTFE film initially formed a localized necking deformation and whitening in the middle. The crystal rotated at tie-chain regions between crystalline and amorphous phases while stretching. For uniaxial stretching, the $\alpha$ phase was mainly determined by the deformation of amorphous region. After the yielding stress stage, the oriented crystal lamellae started separating from each other, causing a non-linear decrease of plastic deformation during the chain
reorientation process. However, this does not happen to samples with stretching ratios above 5 because of the transformation of α phase into β phase \[^{23}\].

![Diagram of semi-crystalline PVDF-BTFE deformations steps](image)

Figure 6-1. The semi-crystalline PVDF-BTFE deformations steps (a) crystal rotation, (b) lamellar separation, (c) plastic deformation, and (d) breaking at different stretching stages \[^{23}\].

As the strain gradually increased, the amorphous regions completely realigned and rotated in the middle of dumbbell. High strain and chain morphology was formed because of the chain realignment. For experiment, the maximum strain of chains was about 550% at the break point of the unstretched film. This ratio is highly dependent on strain rate. After the chain reorientations were completed, causing the hardening of film structure \[^{23}\]. The chain mobility in the polymer was limited because of the strong crystal rotation and chain interaction. In the end, the film broke at the ultimate tensile strength when the stretching force was increased. Split behavior was observed because of fracture at the maximum stress.

One of the common sources of error in this experiment is the stretching rate. The shape of stress-strain diagram can be affected by testing speed. For example, some materials exhibit an appreciable increase in strength with faster test speeds. Also the shape of specimen can affect the measured tensile strength. Improper alignment of grips and the specimen when clamped in the grips can causes errors.
In our opinion, during stretching process, the stacked crystalline lamellae of PVDF-BTFE films would be separated, deformed and reorganized. The imperfect crystals among the lamellae could be easily transformed into b phase under stress. When stretched near 110 °C, the stress induced by stretching is relative high to induce a higher efficiency of a to b phase transformation \(^{[23]}\). When stretched above 120 °C, the stress introduced by stretching become low due to higher chain mobility, which impede \(\alpha\) to \(\beta\) phase transformation. When stretching above 130 °C, the chain mobility of fibers became higher, resulting in the formation of \(\alpha\) form. There is no \(\alpha\) to \(\beta\) phase transformation occurred above 130 °C.

**X-ray diffractometry**

XRD data was collected on a PANalytical Xpert Pro MPD XRD in powder configuration on film samples of 30-40 \(\mu\)m. Stretched sample 1.1 (6% BTFE) and 1.25 (9% BTFE) were tested for crystalline morphology analysis.
Figure 7-1. X-ray diffraction data for P(VDF-BTFE) 94/6mol% as prepared and uniaxially stretched films were measured.

Figure 7-2. X-ray diffraction data for P(VDF-BTFE) 91/9mol% as prepared and uniaxially stretched films were measured.

The XRD pattern of unstretched P(VDF-BTFE) copolymers are consistent with DSC results, the diffraction intensity. The diffraction intensity ratio of crystalline to amorphous phase decreases with increasing BTFE content due to reduction of crystallinity. Copolymer with 6wt% BTFE has 36.7% crystalline, while copolymer with 9 wt% BTFE has 33.6% crystalline. With increasing amount of BTFE, the diffraction peak shifts to higher angle which might due to the increase of $\beta/\alpha$ phase ratio\(^{[19]}\).

As shown in Figure 7-1, 2, addition of small amounts of BTFE co-monomer to VDF leads to polymers with prevalently $\beta$-PVDF structure (higher $\beta/\alpha$ ratios than VDF-CTFE polymer).
For the stretched films, XRD results shows that the \( \alpha \) phase structure is still retained in the polymer. The intensity of the diffraction peak was increased due to the orientation effect and the increase of crystallinity. The peak position of (100) diffraction shifts to a lower angle, which can be explained as expansion of crystal lattice by the bulky BTFE.

The lamellar thickness and crystallite size \( D_{hkI} \), can be estimated from the full width half max (FWHM) of the diffraction peaks. The domain size can be calculated from Scherrer equation:

\[
\text{t, thickness} = 0.9 \frac{\lambda}{(B \cos \theta)}
\]

where \( \lambda \) is wavelength of X-ray, \( B \) is the FWHM of peak (hkl), and theta is peak position. The change of calculated crystallite size \( D_{(110)} \) of stretched P(VDF-BTFE) copolymers is shown in Table. The size \( D_{(110)} \) decreases from 13.2nm for 6wt% BTFE copolymer to about 5.4 nm for the 9wt% BTFE copolymer. As expected, the comonomer BTFE acts as a defect, break up the polarization ordering and reduces the crystallite size of PVDF. Mechanical stretching would increase the crystallite size of \( D_{(100)\alpha} \) and reduces the size of \( D_{(110/200)\beta} \).

<table>
<thead>
<tr>
<th>sample</th>
<th>% X-stal</th>
<th>Crystallite size 100( \alpha ) (Å)</th>
<th>Crystallite size 110/200( \beta ) (Å)</th>
<th>( \alpha ) phase content</th>
<th>( \beta ) phase content</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 unstretched</td>
<td>37.8</td>
<td>92</td>
<td>132</td>
<td>.648</td>
<td>.352</td>
</tr>
<tr>
<td>1.1 stretched</td>
<td>42.96</td>
<td>132</td>
<td>111</td>
<td>.488</td>
<td>.512</td>
</tr>
<tr>
<td>1.25 unstretched</td>
<td>35.01</td>
<td>127</td>
<td>54</td>
<td>.602</td>
<td>.398</td>
</tr>
<tr>
<td>1.25 stretched</td>
<td>38</td>
<td>130</td>
<td>137</td>
<td>.583</td>
<td>.417</td>
</tr>
</tbody>
</table>

The XRD patterns of unstretched and stretched P(VDF-BTFE) copolymer are shown in Figure 7-1, 2. After stretching, PVDF films were transformed into a \( \beta \) phase dominate structure.
Dielectric Properties of P(VDF-BTFE)

-Effect of Stretching

Figure 8-1. Room temperature dielectric constant and loss of P(VDF-BTFE) (6wt% BTFE) unstretched and stretched sample as a function of frequency
The room temperature dielectric constant and loss (\(\tan \delta\)) as a function of frequency for P(VDF-BTFE) (6wt% and 9%wt BTFE) unstretched and stretched sample are shown in Figure 8-2. It can be seen that there is a slight decrease in dielectric constant over all frequencies as samples are stretched. This is unexpected as the stretching orients the dipoles in a way that maximize the field effect. The important thing to realize in this experiment is that we are not only measuring the effect of electric field on the dipoles, but also measuring the effect on ions and other impurities. Since the dielectric response originates mostly from the crystalline phase it is a reasonable assumption that an increase in crystallinity plays a role in the increase of dielectric constant \[^{[20][21]}\]. A more polar structure exists in the stretched sample with higher degree of dipole orientation in the direction of film thickness.

Figure 8-2. Room temperature dielectric constant and loss of P(VDF-BTFE) (9wt% BTFE) unstretched and stretched sample as a function of frequency
The unstretched sample shows higher dielectric loss than the stretched samples at low frequency. This is a sign of conduction and space charge polarization that take place at low frequency range. After sample has been stretched, the space charge polarization and conduction would be blocked by orientation of crystals. The unstretched film develops more of a U-shaped curve while the curve for the stretched film is flat \cite{20,21}. The flatness in terms of loss at low fields indicates that the stretching process reduces the impurities in the polymer. In the frequency range of 104 to 106 Hz, the unstretched sample gives lower dielectric loss because the nonpolar phase possesses a faster relaxation time than the polar phases under an AC electric field.

Based on the loss data, the high dielectric constant of unstretched film is likely a result of impurity motion. As stretching proceed, the impurity motion was eliminated which causes the reduction of dielectric constant.

**-Effect of BTFE content and molecular weight**
Figure 8-3. Room temperature dielectric constant of unstretched P(VDF-BTFE) with 6wt% BTFE and P(VDF-BTFE) with 9wt% BTFE

It is shown in Figure that at room temperature, the dielectric permittivity ($\varepsilon'$) of PVDF copolymer with 6% and 9% BTFE are 10.6 and 11.2 respectively at 1 kHz. The high molecular weight polymers (6% BTFE) possess a similar dielectric loss (tan delta) near 1 kHz. Above 10 kHz, tan delta begins to rise rapidly due to the dipolar relaxation in the polymer. The low molecular weight polymer shows higher loss than high molecular weight polymer above 10 kHz. This is due to its higher crystallinity and more polar domain phase. Higher dielectric loss at frequencies below 1 kHz has been observed in higher molecular weight polymers (6% BTFE) compared to that in polymer with 9% BTFE. This is ascribed to the higher inter- and intra-molecular relaxation times associated with the higher molecular weight polymers. The
dipolar contribution to permittivity decreases as frequency increases, causing the decreased dielectric permittivity.
Chapter 5

Conclusions and Future Work

A study of the effects of uniaxial stretching on the structure and dielectric properties of P(VDF-BTFE) has produced some useful information. From the structure point of view, bulky comonomer BTFE act as defects in the crystal structure of PVDF. These defects can expand the inter-chain space of the crystals and stabilize the nonpolar phase.

Semi-crystalline PVDF-BTFE copolymer in the b-phase have been studied by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), gel permeation chromatography (GPC) and LCR meter. The WAXD data of the stretched PVDF-BTFE films showed evidence of a phase transformation into the b-phase via stretching. The applied strain to the film results in alignment of polymer chains into the crystals so that all-trans planar zigzag (TTT) conformation was introduced into the polymers. The uniaxial stretching leads to longitudinal deformation of polymer chains in the crystal.

Mechanical stretching was found to promote a partial conversion of the primarily non-polar a crystalline structure to the more polar b phase. A detailed structural analysis on P(VDF-BTFE) utilizing different XRD techniques suggests the existence of both non-polar and polar phases in the stretched films. As expected, the crystalline structure can be converted to a more polar phase as the stretching ratio is increased. However, the nonpolar to polar phase conversion is not as good as homopolymer due to the bulky BTFE defects in the copolymer.

The processing conditions greatly influence the morphology and phase content of PVDF-BTFE copolymer. The maximum b-phase content was obtained at a stretch ratio of 5 at 110 °C. The stretch ratio affects the phase transformation more than the stretching temperature. The chain ordering and disordering in crystallites during film stretching is responsible for the transformation of polymer crystals from a to b phase. For higher draw ratios the polymer chain get more oriented and crystal structure become more
packed. DSC results show stretching causes a decrease in melt temperature and an increase in crystallinity for both copolymer samples which is due to the formation of small crystals in the amorphous phase. Measurement of dielectric constant as a function of frequency shows that stretching reduces the permittivity in both materials. The results also show that initial stretching is successful in reducing losses due to a decrease in conduction which will improve energy storage efficiency. There is a strong correlation between polymorphism, crystal structure, molecular weight, and energy storage efficiency for both copolymers.

The study of dielectric and ferroelectric materials with high energy density will be continued for the energy storage design. As shown in this study, the range of work in this thesis has illustrated the importance of structure-property relationships in the P(VDF-BTFE) ferroelectric polymers. We show that modification of the chemical structure of PVDF through defects/structure modification can be utilized to give an excellent electromechanical response. The significance of chemical structure, modified by processing on the dielectric properties is demonstrated. The knowledge of the structure-property relationships from here would lead to the development of ferroelectric polymers with new chemical and crystalline structure useful for a variety of applications in the healthcare, military and industrial technologies.
Chapter 6

ABET thesis consideration

-Economic issues

For the polymerization process, the startup cost for Ethyl hydroxyl cellulose (EHEC) is $4.6/kg. Ethyl hydroxyl cellulose (EHEC) was used as received from Polymer Lab Inc. Tetrahydrofuran (THF) was distilled from sodium benzophenoneketyl under Argon protection. Vinylidene fluoride and bromotrifluoethylene were purchased from SynQuest Laboratory Inc. The cost required for small scale production of PVDF-BTFE film is in the $100-200 per pound range \cite{14}. The related energy cost is in the $10-20 per month range.

-Environmental Issues

Vinylidene fluoride is used as starting material in manufacture of PVDF copolymers. It is a colorless flammable gas with a faint ether-like odor under room temperature and pressure. VDF is produced and polymerized in a closed system. Emissions will be incidental during maintenance operations. Potential exposure to VDF gas is limited to industrial settings \cite{14}. The Vinylidene fluoride is consumed in the polymerization process. It is unlikely that any significant amount of VDF remains in the final product. Therefore consumer exposure is not expected.

VDF gas is not expected to be released to the environment during production process or transportation. VDF is a flammable gas and can form explosive mixtures with air.

-Sustainability

The technology of PVDF-BTFE polymerization is sufficiently mature to ensure its success. PVDF is usually synthesized from the gaseous VDF monomer via free-radical polymerization process.
This is followed by melt casting which is first developed in 1970. Melt processing of fluoropolymers is usually under high temperatures, mainly to lower viscosity to improve flow. Any decomposition as a result of elevated temperature exposure may produce gases and generate pressure in the absence of air vent.

PVDF-BTFE copolymers used in this experiment are thermoplastics and can be reused under right circumstances. Most melt-processible polymer can be reprocessed in a fashion similar to other thermoplastics. Recycling of fluoroplastics involves re-extrusion, filtration and cleaning of these polymers\textsuperscript{[14]}.

-Ethical Issues

Creating chemicals usually means creating toxic byproduct which might have impact on people and natural resources\textsuperscript{[15]}. Market demand accelerates product development without allowing time to determine long-term effects of exposure. In our case, Tetrafluoro-ethylene (TFE) might cause acute effects when inhaled, including irritation of upper respiratory tract, mild depression of central nervous systems. All of the experiments for the thesis were conducted under the operation of air vent. An exposure limit of 5 ppm has been established for laboratories and industries\textsuperscript{[15]}. We perform services only in the area of our competence. We also try to avoid conflicts and showed respect to intellectual properties of other individuals.

-Health and Safety

The tetrafluoro-ethylene (TFE) might causes effects when inhaled, including irritation of upper respiratory tract and mild depression of central nervous system. Massive exposure produces cardiac arrhythmia and cardiac arrest.
Toxicity studies indicate vinylidene fluoride (VDF) does not irritate skin, eyes or the respiratory system. Inhalation studies indicate that vinylidene fluoride has a very low toxicity profile. Under industrial settings, contact with liquefied VDF can cause frostbite \[15\]. It may emit toxic fumes when involved in fire. VDF can undergo unintentional decomposition under certain industrial conditions. VDF and TFE monomer is not expected to be intentionally released to the environment during processing or transportation.

\textbf{-Social and Political Issues}

Copolymers of PVDF are commonly used in piezoelectric and electrostrictive applications. The economic security of United States requires development of renewable energy sources. The storage of electric power is essential to both these objectives \[15\]. There are number of political barriers to implementing new systems. Power companies argue that federal and state government should support research until it has been shown to be economically feasible. There is a need for a central panel to coordinate efforts and also to recommend regulatory rules to facilitate the development of energy storage systems.
References


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Strategic Polymer Sciences, Inc.  (Advisor: Dr. Qiming Zhang)  State College, PA
Assistant Research Engineer  July 2011—January 2012
  ▪ Assisted senior engineers in the research and development of electro active polymers technology for high energy density capacitor films.
  ▪ Conducted curing experiment on several fluoropolymers to investigate the effect of curing temperature and time on its properties.
  ▪ Developed a scope study, characterized the P(VDF-HFP) copolymer and (VDF-TrFE-HFP) terpolymer by variety of methods to determine its mechanical and electrical properties.
  ▪ Gained experience in curing, film processing, DSC, DMA and dielectric measurement.

Sino Oil King Shine Chemical Co., LTD  Langfang, China
Laboratory Assistant  May 2010—August 2010
  ▪ Conducted organic synthesis of polyhexadecyl acrylate (PA-16) and polyoctadecyl acrylate (PA-18) for production test for diesel pour point depressant
  ▪ Gained experience in FTIR, 2D-NMR, GPC, MFI (Melt Flow Index), viscosity measurement, and polymer synthesis.

Material Research Laboratory (MRL)  State College, PA
Undergraduate Research Fellows  October 2009—April 2010
  ▪ Determined and investigated the mechanical properties and crystal structure of several \( A_3B_{11} \) type metal alloy compound using X-ray powder diffractometer.
  ▪ Gained experience in failure analysis, SEM, X-ray diffractions, CrystalMaker software.

Honors & Awards:

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