Advanced Ferroelectric and Related Electromechanical Polymers

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Abstract

This talk will cover two classes of electroactive polymers under development recent at Penn State. One is the modified poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) polymer and the other is the high dielectric constant all-organic composite. Recently, making use of the defect structure modification in P(VDF-TrFE) based polymers, we converted normal ferroelectric P(VDF-TrFE) into relaxor ferroelectric polymer. This new class of polymer exhibits very high electrostrictive strain (~7%) with high elastic energy density (~1 J/cm^3), attractive for actuators and electromechanical transducers. In addition, it also possesses a high room temperature dielectric constant (~60) which opens up possibilities for high performance polymer based dielectric devices. This talk will discuss those features and the approaches taken to modify the P(VDF-TrFE) based polymers, i.e., the high-energy electron irradiation and terpolymer approaches. One of the challenges in further improving the performance of electroactive polymers driven by external field is how to significantly raise the dielectric constant. Although the modified PVDF based polymer exhibits the highest room temperature dielectric constant (60 versus below 10), it is still far below those in the inorganic materials. This talk will present experimental results showing the potential of using delocalized electrons in conjugated bonds to achieve ultrahigh dielectric response in polymer-like materials or conductive polymers, where an all-organic composite with a dielectric constant near 1000 can be achieved. As a result, a strain of near 2% with an elastic energy density higher than 0.1 J/cm^3 can be induced under a field of 13 V/μm.

I. Introduction

Polymer based materials have attracted a great deal of attention and have found many applications for electromechanical devices to perform energy conversion between the electric and mechanical forms such as artificial muscles, smart skins for drag reduction, actuators for active noise and vibration controls, and micro-fluidic systems for drug delivery and micro-reactors [1-4]. Polymers are renowned for their excellent mechanical properties including lightweight, flexible, and easy processing, and that polymers can be conformed to complicated shapes. On the other hand, compared with inorganic materials, the electromechanical responses of polymer-based materials are quite low. Especially, one of the unique features of the polymers, that is, most polymers can withstand very high strain (>10%) without fatigue, which is not possible in inorganic materials, has not been utilized to develop electroactive polymers with ultra-high electroactive strain responses.

In polymeric materials, there are many unique features and phenomena which can be made use of to generate high electromechanical responses. For example, in P(VDF-TrFE) copolymers, experimental evidence has shown that there are large strains (~10%) accompanying the phase transformation process between the ferroelectric and paraelectric (F-P) phases [5]. The origin of such a large strain in the F-P transition is due to the molecular conformation change [6]. In the ferroelectric phase, the molecules take the all trans conformations, while in the paraelectric phase, the molecular conformation takes the form of a mixture of trans-gauche (TGTG') and T_3GT_3G' conformations. When the molecular conformation changes from the all trans to TGTG' and T_3GT3G' conformations, a large dimensional change occurs. Due to the ferroelastic coupling in P(VDF-TrFE) copolymer, such type of conformation change can be induced by electric fields at temperatures above the F-P transition. Furthermore, at temperature regions just above a first order F-P transition, a polar-phase can be electrically induced. It has been shown that in this field induced phase, a very large electromechanical coupling factor, which measures the electromechanical conversion efficiency, can be achieved (theoretically ~ 100%) [6]. For P(VDF-TrFE) copolymers, it is well known that the F-P transition is first order in nature.

All these observations suggest that by operating the P(VDF-TrFE) copolymers at near F-P transition region, very high electromechanical responses may be realized. On the other hand, there are problems which are common to all the first order phase transformation process in polymers, i.e., large hysteresis, narrow transition temperature region, and that the temperature range of the transition is far above room temperature, and all of which are not desirable for practical applications. In order to overcome these problems, P(VDF-TrFE) based polymers have to be modified. In this study, P(VDF-TrFE) based polymers are modified via two approaches: the high energy electron irradiation (HIEEP) and copolymerizing the P(VDF-TrFE) with a small amount of third chlorinated monomer to form a terpolymer [7-9]. Several effects occur when the defects are introduced into the ferroelectric crystalline region of the polymer. First of all, the defect structures weaken the inter- and intra-chain dipolar coupling and hence, lower the F-P transition to near room temperature. In addition, these defects also introduce inhomogeneity in the ferroelectric phase which broadens the transition region. Furthermore, they reduce and in some cases eliminate the energy barrier in the transformation between different molecular conformations which in turn

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reduce or eliminate the hysteresis associated with the transformation. As a result, the normal ferroelectric P(VDF-TrFE) copolymer is transformed into a relaxor ferroelectric polymer with a high electrostriction and improved the electromechanical coupling factor [7-9].

One of the challenges in further improving the performance of electroactive polymers driven by external field is how to significantly raise the dielectric constant. Although the modified PVDF based polymer exhibits the highest room temperature dielectric constant (60 versus below 10), it is still far below those in the inorganic materials. By using delocalized electrons in conjugated bonds to achieve ultrahigh dielectric response in polymer-like materials or conductive polymers, recently we developed an all-organic composite with a dielectric constant near 1000 can be achieved. As a result, a strain of near 2% with an elastic energy density higher than 0.1 J/cm^3 can be induced under a field of 13 V/μm [10].

This paper will review these recent works, including the high-energy irradiated electrostrictive P(VDF-TrFE) based copolymers, P(VDF-TrFE) based terpolymer without irradiation and all organic composites. In addition, issues related to the development of high performance electroactive polymers will also be discussed.

II. Experiment

The copolymer was purchased from Solvay and Cie of Belgium. The copolymer films were fabricated from solution casting (Dimethylformamide was used as solvent). In this investigation, both non-stretched and uniaxially stretched films were prepared. The uniaxial stretching of the films was carried out at room temperature and the films were stretched to 5 times of the original length. Before irradiation, the films were annealed at a temperature below the melting transition to improve the crystallinity. For the unstretched films, the annealing was carried out at 135 °C for 12 hrs. For the stretched films, it was found that by adopting a two step annealing process, the field induced strain along the stretching direction can be improved [11]. In this two step annealing process, the films were annealed at 120 °C for 2 hrs to release the stress stored in the films due to the stretching and then annealed at 134 °C for 2 hrs to improve the crystallinity. The irradiation was carried out in a nitrogen atmosphere at 100 °C using the electrons with an energy of 1.2 MeV. The irradiation dose used in this investigation was 0, 10, 20, 35, 50, 65, 75, 85, 100, and 175 Mrads, respectively. From the experimental data, it was found that the HIEEP of 68/32 mol% irradiated with 75 Mrads dose exhibits the highest electromechanical response among all the HIEEPs investigated.

The terpolymers were prepared by a combination of the suspension polymerization process with an oxygen-activated initiator. Two terpolymers were synthesized and investigated: P(VDF-TrFE-CFE) 62/38/4 mol% and 68/32/9 mol%. To facilitate the discussion and comparison with the irradiated P(VDF-TrFE) copolymer, the composition of the terpolymer is labeled as VDF$_x$-TrFE$_{1-x}$-CFE$_y$, where the mole ratio of VDF/TrFE is x/1-x and y is the mol% of CFE in the terpolymer. The polymer films were prepared using the solution cast method with dimethylformamide (DMF) as the solvent. The films were annealed at a temperature near 115 °C to improve the crystallinity.

Composite films were prepared using the solution cast method. P(VDF-TrFE) copolymer was dissolved in dimethylformamide (DMF) and then a proper amount of CuPc powder was added to the solution. The solution was ultrasonically stirred to disperse the CuPc powder. After that, the solution was poured onto a glass plate and dried at 70 °C. The typical film thickness was about 40 μm. The composites were also irradiated at 100 °C with 1.2 MeV electron to convert the copolymer matrix into an electrostrictive polymer with an improved room temperature dielectric constant. By using the terpolymer as matrix, composite films can also be prepared without irradiation.

The typical film thickness used in this investigation is 20 μm. For electrical characterization, gold film of 40 nm thick was sputtered on both sides of copolymer film to serve as electrodes. The polarization hysteresis loop was measured at 1 Hz. The strain along the thickness direction (longitudinal strain) and the strain along the length direction (transverse strain) were measured by using a photonic sensor. All the strain responses were measured under a 1 Hz AC electric field.

III. Defects Modified P(VDF-TrFE) Based Polymers

By means of high-energy electron irradiation and copolymerizing the P(VDF-TrFE) with a small amount of third monomer to form a terpolymer, defects were induced into the ferroelectric crystalline region of the polymer, thus the irradiated copolymer and terpolymer without irradiation are classified as defects modified P(VDF-TrFE) polymers. As a result, the normal ferroelectric copolymer is transformed into a relaxor ferroelectric polymer with a high electrostriction and improved the electromechanical coupling factor. Figure 1 compares the dielectric responses between the normal ferroelectric P(VDF-TrFE) copolymer, a high energy electron irradiated copolymer, and a terpolymer. It is evident that the dielectric peak, which is associated with F-P transition in the normal ferroelectric P(VDF-TrFE) copolymer, is broadened markedly and moved to near room temperature for the irradiated copolymer and the terpolymer. In addition, in the defect structure modified polymers (the terpolymer and irradiated copolymer) the broad dielectric peak position shifts with the frequency f as illustrated in figure 1, which can be described quite well by the Vogel-Folcher (V-F) law (figure 1(d)), $f = f_0 \exp[\frac{-U}{k(T_m - T_f)}]$, where U is a constant and k is the Boltzmann constant, T_f can be regarded as the freezing temperature, corresponding to the peak temperature of the static dielectric constant (~ 0 Hz frequency), and the pre-factor f_0 is the upper frequency limit of the system, corresponding to the dipolar response when there is no coupling between the dipolar units in the system. Such a behavior is a typical feature to all the known relaxor ferroelectric materials [12].

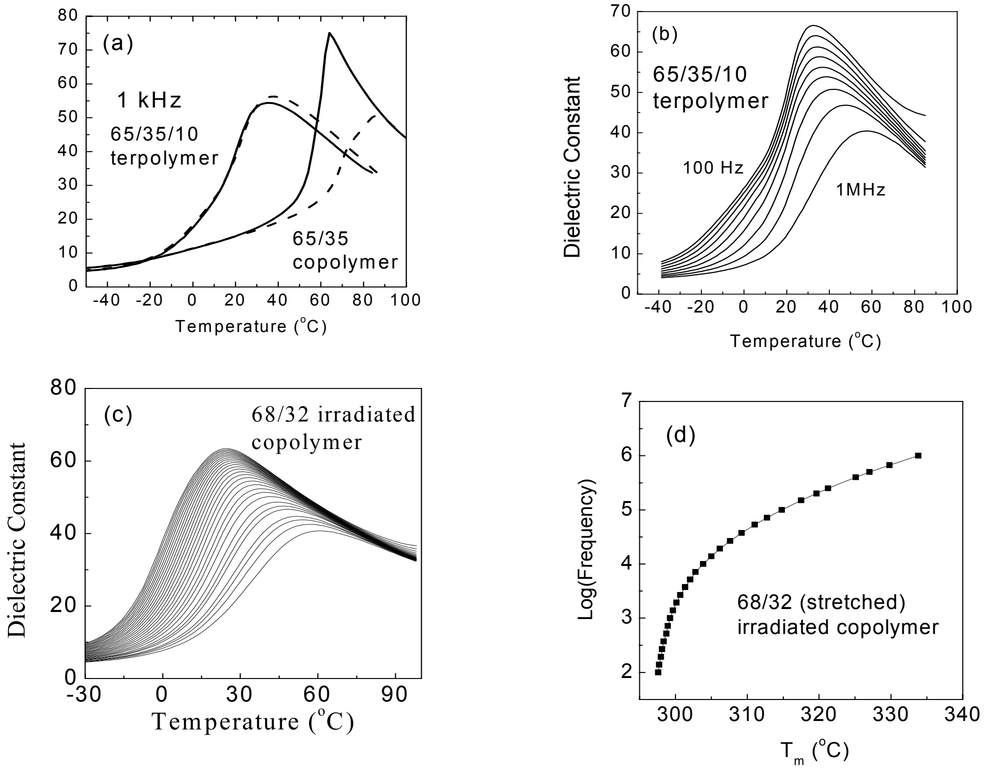

Fig. 1: Comparison of the dielectric constant of (a) the P(VDF-TrFE) 65/35 copolymer (at 1 kHz), (b) the irradiated P(VDF-TrFE) 68/32 mol%, and (c) the terpolymer of P(VDF-TrFE-CFE) 62/38/4 mol%. The terpolymer and irradiated copolymer data are measured in the frequency range from 100 Hz to 1 MHz and the data show that the dielectric peak temperature shifts with frequency. (d) The fitting of the dielectric data (dots) to the V-F law (solid curve).

A. High Energy Electron Irradiated Copolymers

Presented in Figure 2(a) is the field induced strain along the film thickness direction (longitudinal strain S_3) for the non-stretched HEEIP films irradiated with 75 Mrads dose where –5% strain is induced under a field of 150 MV/m. The plot of strain versus the square of the polarization P_3 yields a straight line, indicating that the response is electrostrictive in nature ($S_3=Q_{33}P_3^2$, Figure 2 (b), where Q_{33} is an electrostrictive coefficient). For the irradiated copolymer, Q_{33} is found in the range between –4 to –15 m^2/C, depending on the sample processing conditions.

For unstretched films, the transverse strain is relatively small (~1% level under 100MV/m field) and the amplitude ratio between the transverse strain and longitudinal strain is less than 0.33 [13]. This feature is attractive for devices utilizing the longitudinal strain such as ultrasonic transducers in the thickness mode, and actuators and sensors making use of the longitudinal electromechanical responses of the material. On the other hand, for stretched films, a large transverse strain (S_1) along the stretching direction can be achieved as shown in Figure 2(c), where the transverse strain of more than 4% can be achieved under a field of 80 MV/m for a stretched copolymer film irradiated with 75 Mrads.

For electroactive materials, in addition to the induced strain level, the elastic energy density, which measures both the stress and strain generation capability of the material, and electromechanical coupling factors, which measure the electromechanical energy conversion efficiency of the material, are other two important parameters. For a linear elastic material, the volumetric elastic energy density is ½ YS^2, where Y is the elastic modulus and S is the strain, respectively. For the stretched films, the elastic energy density corresponding to the actuation along the stretching direction is 1 J/cm^3, which is near 10 times larger than that achievable in the traditional piezoelectric ceramics [7].

For electrostrictive materials, the electromechanical coupling factor *(k_{ij})* has been derived by Hom et al. based on the consideration of electrical and mechanical energies generated in the material under an external field [14]:

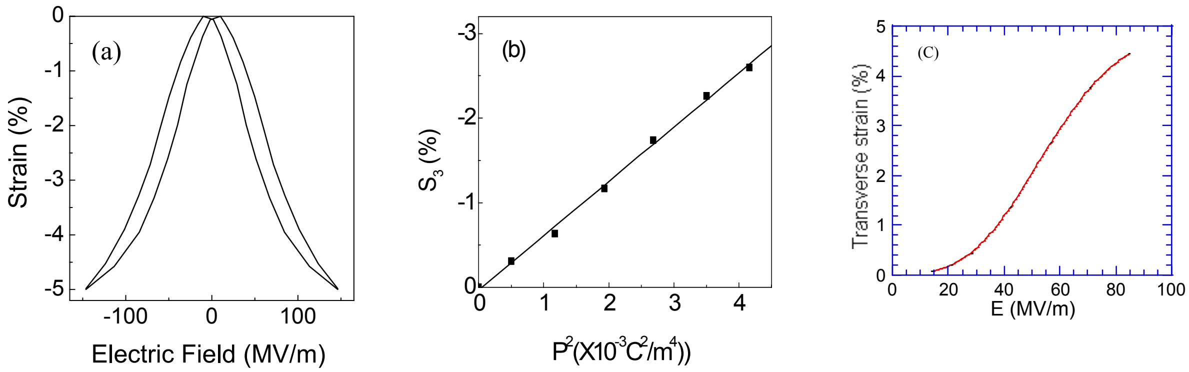

Fig. 2: (a) The longitudinal strain as a function of the applied field measured at room temperature for irradiated P(VDF-TrFE) 68/32 mol% copolymer, (b) The longitudinal strain versus the square of the polarization where the data points are shown and the solid line is the fitting of strain versus the square of the polarization, (c) The transverse strain for the irradiated P(VDF-TrFE) 68/32 mol% stretched copolymer film (the strain is measured along the film drawing direction).

$$k_{3i}^2 = \frac{kS_i^2}{s_{ii}^D\left[P_E \ln\left(\frac{P_S+P_E}{P_S-P_E}\right) + P_S \ln\left(1-\left(\frac{P_E}{P_S}\right)^2\right)\right]} , \qquad (1)$$

where i=1 or 3 correspond to the transverse or longitudinal direction (for example, k_{31} is the transverse coupling factor) and s_{ii}^D is the elastic compliance under constant polarization, S_i and P_E are the strain and polarization responses, respectively, for the material under an electric field E. The coupling factor depends on E, the electric field level. The constant k in eq. (1) is defined from the polarization-field (P-E) relationship:

$$|P_E| = P_S \tanh(k|E|) \qquad (2)$$

where P_S is the saturation polarization and k is a constant.

Combining the strain data with the polarization and elastic modulus data, the electromechanical coupling factors for the irradiated copolymers can be obtained as shown in Figure 3. Near room temperature and under an electric field of 80 MV/m, k_{33} can reach more than 0.3, which is comparable to that obtained in a single crystal P(VDF-TrFE) copolymer [15]. More interestingly, k_{31} of 0.65 can be obtained in the stretched copolymer, which is much higher than the values in unirradiated P(VDF-TrFE) copolymers and, to our knowledge, is the height among all the known ferroelectric, piezoelectric, and electrostrictive polymers [3].

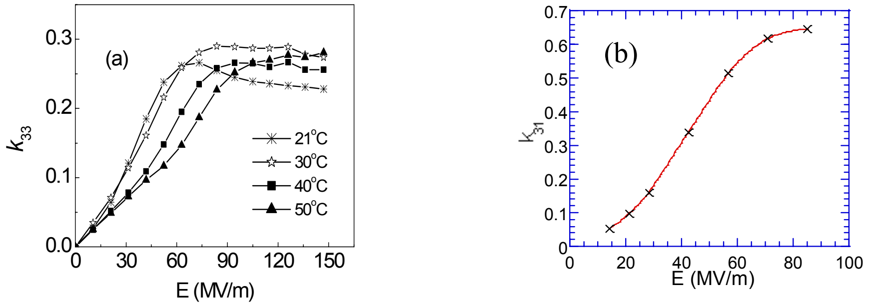

Fig. 3: (a) The longitudinal k_{33} at different temperatures and (b) room temperature transverse k_{31} electromechanical coupling factors for irradiated 68/32 copolymer films. Data points are shown and solid curves are drawn to guide eyes.

B. P(VDF-TrFE) Based Terpolymer

Although high energy irradiations can be used to convert the normal ferroelectric P(VDF-TrFE) into a relaxor ferroelectric with high electrostriction, the irradiations also introduce many damages to the copolymer, for instance, the formation of crosslinking, radicals, and chain scission [16,17]. From the basic ferroelectric response consideration, the defects modification of the ferroelectric properties can also be realized by introducing randomly in the polymer chain a third monomer, which is bulkier than VDF and TrFE. Furthermore, by a proper molecular design which enhances the degree of molecular level conformational changes in the polymer, the terpolymer can exhibit much higher electromechanical response compared with the high energy electron irradiated copolymer.

The introduction of termonomer would favor the gauche conformation rather than all-trans conformation. That is, the intra-chain interaction (Columbic force between hydrogen and substituents in the monomer) should be strong. The termonomer should possess a relative large size to increase the inter-chain space that would reduce the electric field required to transfer the polymer from paraelectric to ferroelectric phase. In addition, the third monomer should easily crystallize with VDF and TrFE in order to increase the crystallinity since the electromechanical properties in this class of polymers originate from its crystal regions. Actually, the phase diagram of P(VDF-TrFE) system also shows some clues regarding these. For pure PVDF, the nonpolar structure (more gauche conformation) rather than polar structure (all-trans conformation) is formed in polymer as made. In order to transfer the PVDF from paraelectric to ferroelectric phase, a mechanical drawing or applying an extremely high electric field (~500 MV/m) is required. If the content of TrFE is higher than 20 mol%, the P(VDF-TrFE) copolymer is at ferroelectric phase at room temperature. Comparison to TrFE, the intra-chain interaction in VDF is much stronger. Therefore, the PVDF exhibits a structure corresponding to paraelectric phase. However, since the size of VDF is small, an extremely high field is needed to transfer the polymer from paraelectric to ferroelectric phase. For the convenience of discussion regarding the fluoromonomers, the commercially available fluoromonomers are listed in Table I. The size of PMVE is the biggest among other monomers listed in Table I. Since PMVE is too big, it is hard to crystallize with VDF and TrFE. The terpolymers, such as P(VDF-TrFE-HFP) and P(VDF-TrFE-CTFE), were studied previously [18]. It is found that the electromechanical performance of these terpolymers is much better than that of piezoelectric P(VDF-TrFE) copolymer and even comparable with the high-energy electron irradiated P(VDF-TrFE) copolymer. Although the strain response level of P(VDF-TrFE-HFP) is close to that of P(VDF-TrFE-CTFE), the hysteresis of P(VDF-TrFE-HFP) is clearly higher than that of P(VDF-TrFE-CTFE). However, for the same electric field induced strain level, the electric field required in P(VDF-TrFE-HFP) is smaller than that in P(VDF-TRFE-CTFE). The reason behind these phenomena is that the HFP is too big. That is, although a smaller field is required to achieve the same strain level due to a large termonomer, the hysteresis is increases due to the rotation of large group of CF3 in HFP. The major draw back of these terpolymers is its relative low Young's modulus that is related to the low crystallinity due to the big size of termonomer. All these indicate that in order to further improve the electromechanical performance of P(VDF-TrFE) based terpolymer the third monomer should possess a smaller size than CTFE to increase crystallinity. Based on these results, CFE was chosen for this study.

Table I: Commercially Available Fluoromonomers

Fluoromonomers	Abbreviation	Monomer Structure
Vinyl fluoride	VF	CH_2=CHF
Vinylidene fluoride	VDF	CH_2=CF_2
Trifluoroethylene	TrFE	CHF=CF_2
Tetrafluoroethylene	TFE	CF_2=CF_2
Chloro-fluoroethylene	CFE	CH_2=CFCl
Chlorotrifluoroethylene	CTFE	CF_2=CFCl
Hexafluoroprolylene	HFP	CF_2=CF-CF_3
Perfluoro(Methyl vinyl ether)	PMVE	CF_2=CF-O-CF_3

Presented in Figure 4(a) is the field-induced strains along the thickness direction (S_3) as a function of the applied electrical field for the terpolymer P(VDF-TrFE-CFE) 62/38/4 mol%. Under a field of 130 MV/m, a thickness strain of – 4.5% can be achieved, which is comparable to that observed in HEEIP. Because of higher crystallinity in this P(VDF-TrFE-CFE) terpolymer (as determined by the DSC data), the elastic modulus Y~1.1 GPa for this unstretched film is much higher than that of HEEIP which is about 0.4 GPa for unstretched films, resulting in a higher elastic energy density, $YS^2/2$, ~1.1 J/cm^3. The longitudinal coupling factor k_{33} is presented in Figure 4(b). It is interesting to note that the coupling factor can reach more than 0.55 which is far above coupling factors reported in all known piezoelectric and electrostrictive polymers [3]. By increasing the ratio of VDF/TrFE in the terpolymer, the field induced strain level can be raised owing to the fact that the lattice strain between the polar conformation and non-polar conformations increases with the VDF/TrFE ratio (see Figure 5) [13]. Presented in Figure 6(a) is the thickness strain of the P(VDF-TrFE-CFE) terpolymer at composition of 68/32/9 mol% and a thickness strain of more than 7% can be reached, which is by far the highest among all the HIEEPs and terpolymers investigated [8, 9,19]. The results here demonstrate the potential of the terpolymers in achieving very high electromechanical responses by composition optimization.

The transverse strain response of this terpolymer was also characterized. Presented in Figure 6(b) is the transverse strain S_1 from the unstretched films and the terpolymer exhibits a much smaller transverse strain compared with the longitudinal strain. Under 100 MV/m, the transverse strain for the unstretched films is only 1%, which results in a very small ratio of the transverse strain to the thickness strain, ~0.23. This is smaller than that for the irradiated copolymer (this ratio for the irradiated copolymer is about 0.33 or less, which by itself is already quite small). The observed difference between the two polymers may lie in the polymer structures, most probably due to the crosslinking in the irradiated copolymers which enhances the correlation in the mechanical deformation between the thickness direction and the lateral direction, compared with non-crosslinked terpolymers.

In sharp contrast to the irradiated copolymers, in which by uniaxial stretching, the transverse strain along the stretching direction becomes quite large (comparable to the thickness strain), the transverse strain along the stretching direction for the terpolymer P(VDF-TrFE-CFE) 68/32/9 mol% is not very high, as shown in Figure 6(c). Under a field of 120 MV/m, the transverse strain is about 3%, which is much smaller than the thickness strain in the terpolymer and also the transverse strains in the stretched HIEEPs.

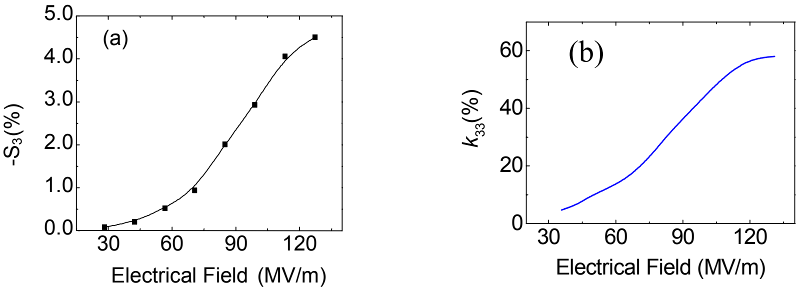

Fig. 4: (a) The field induced longitudinal strain (S_3) as a function of the applied field and (b) The longitudinal coupling factor k_{33} for the P(VDF-TrFE-CFE) 62/38/4 mol% terpolymer versus the applied field amplitude.

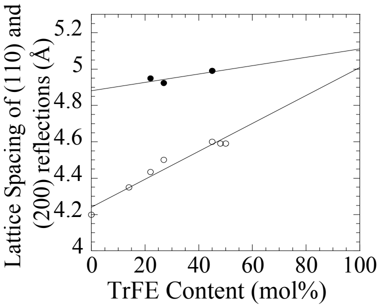

Fig. 5: The lattice strain change through the F-P transition perpendicular to the polymer chain as a function of TrFE mol%. Data points are shown and solid lines are drawn to guide eyes.

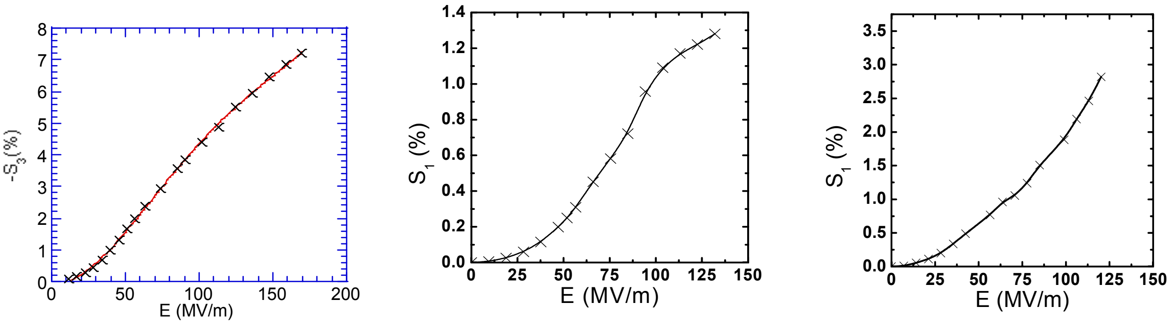

Figure 6. (a) The field induced longitudinal strain (S_3) and (b) transverse strain as a function of the applied field for the unstretched terpolymer P(VDF-TrFE-CFE) 68/32/9 mol%. (c) The transverse strain along the stretching direction for the stretched terpolymer P(VDF-TrFE-CFE) films of 68/32/9 mol% composition.

Table II summarizes and compares the electromechanical properties of four different types of P(VDF-TrFE) based polymers, that is, the normal piezoelectric P(VDF-TrFE) copolymer, HEEIP, P(VDF-TrFE-CFE) terpolymers studied here, and P(VDF-TrFE-CTFE) terpolymer (CTFE: chlorine-trifluoroethylene) [18]. Obviously, the terpolymer with CFE as a modifier shows the highest electromechanical responses.

Table II. Comparison of the electromechanical properties of the modified PVDF based polymers and piezoelectric P(VDF-TrFE).

Polymer		S_M (%)	Y (GPa)	$YS_M^2/2$ (J/cm^3)	k_{33}	k_{31}
PiezoP(VDF-TrFE)		0.2	3.3	0.0066	0.27	
HEEIP	S_3	-5	0.4	0.5	0.30	
	S_1	4.5	1.0	1.0		0.65
P(VDF-TrFE-CTFE)		-4	0.4	0.32	0.28	
P(VDF-TrFE-CFE)						
62/38/4 mol%	S_3	-4.5	1.2	1.2	0.55	
68/32/9 mol%	S_3	-7	0.3	0.73		

*S_M is the strain and $YS_M^2/2$ is the volumetric elastic energy density, Y is the elastic modulus along the actuation direction, and k_{33} is the longitudinal and k_{31} is the transverse electromechanical coupling factors.

IV. An all-organic high dielectric constant composite

For the polymers presented in the preceding section, although the large strain and large elastic energy density achieved represent a breakthrough in improving the electromechanical response of polymers, the high electric field (> 100 MV/m) required to generate the high strain and high elastic energy density may limit the applications of these polymers. The high operation field required to generate high strain and high elastic energy density in these polymers in fact has its origin from the principle of energy conservation. To illustrate this point, we take, as an example, an electroactive polymer which is assumed to be a linear dielectric and elastic material. The stored elastic energy density when a polymer is strained is $U_S = ½ Y S^2$, where Y is the Young's modulus and S is the strain. For an electroactive polymer, the total elastic energy density from all the strains generated cannot exceed the input electric energy density because of the energy conservation. As a linear dielectric material, this input electric energy density from the external electric source is $U_E = ½ K\varepsilon_0 E^2$, where E is the applied field, ε_0 is the vacuum dielectric permittivity (=$8.85\text{x}10^{-12}$ F/m), and K is the dielectric constant of the polymer. In most of the polymeric materials, the dielectric constant k is less than 10, which is far below those in the inorganic materials, many of which can reach more than 5,000. Therefore, in order to generate a high input electric energy density which can be converted to strain energy, a high electric field is required. For example, to generate a strain energy density of 0.1 J/cm^3, which is the elastic energy density in piezoceramics [7], in a polymer with a dielectric constant 10, assuming a 50% energy conversion efficiency, which is very high for the current electroactive polymers, the field required is 67 V/μm. Although it was recently reported that a high induced strain (~ 4%) can be generated in a liquid crystal elastomer under a low field (~1.5 V/μm), however, the elastic modulus of the elastomer is quite low (~ 1 MPa) which results in a very low elastic energy density (~0.001 J/cm^3) [19]. Therefore, in order to reduce the applied field substantially in the electroactive polymers while retaining the high elastic energy density, which is required in many practical applications, one has to substantially raise the dielectric constant of this class of polymers.

In the past, the composite approach, in which high dielectric constant particulates are added to a polymer matrix to form a composite, has been employed to raise the dielectric constant of polymer based materials [20]. However, because these high dielectric constant fillers (most often, ceramic materials) also possess an elastic modulus that is much higher than that of polymers, the resulting composite also shows an elastic modulus much higher than that of the polymer matrix and loses its flexibility. In addition, the low dielectric constant of the polymer matrix utilized (≤ 10) also results in the composite dielectric constant still below 100.

Recently, we experimented with composites using the high dielectric constant organic solids as the filler and the electrostrictive P(VDF-TrFE) as the matrix. In several semiconductor organic solids, very high dielectric constant has been reported [21-23]. One example is copper-phthalocyanine (CuPc) which exhibits a dielectric constant as high as 10^5. The large dielectric constant can be explained in terms of the electron delocalization within CuPc molecules. CuPc oligmers are highly conjugated and have a large planar structure. The easy displacement of the electrons under electric fields from the conjugated π-bonds within the entire molecule and also between neighboring molecules results in a large displacement of the charges within the organic solid and, hence, a high polarizability and high dielectric response. Furthermore, the open molecular structure of the oligmers and the weak van der Waals intermolecular forces render the molecular solids formed with an elastic modulus not much higher than the polymer matrix. On the other hand, CuPc solids are difficult to process and show a high dielectric loss due to the long range intermolecular hopping of electrons. Therefore, in addition to provide a matrix to the CuPc particulates, the polymer matrix also forms insulation layers to significantly reduce the dielectric loss.

The electrostrictive P(VDF-TrFE) polymers are used as the polymer matrix. As has been shown in the preceding sections, the electrocstrictive P(VDF-TrFE) polymers exhibit a high room temperature dielectric constant (>50) which is by far the highest among the all known polymers. Moreover, the polymers also exhibit a very high electrostrictive strain. Both features are highly desirable for the composites.

In deeded, the resulting composite exhibits almost the same elastic modulus as the polymer matrix and but still retains the flexibility. For composites containing 40 wt% to 55 wt% of CuPc, which is the composition range of interest, the elastic modulus at room temperature is in the range of 0.6 GPa to 1.2 GPa, (the density of CuPc is similar to P(VDF-TrFE) and hence the wt% is also similar to the volume %). The composite also exhibits a high dielectric constant as shown in figure 7(a). For comparison, Fig. 7(b) presents the dielectric constant of the polymer matrix. More importantly, a high field induced strain can be induced with a much reduced applied voltage. Presented in figure 7(c) is the field induced strain as a function of the applied field amplitude measured on a composite with 40 wt% CuPc in an electrostrictive P(VDF-TrFE) polymer matrix. A strain near 2 % at room temperature can be induced under a field of 13 V/μm and the strain measured is proportional to the applied electric field. At higher temperature, such as 50°C, much higher strain (1.2%) is observed at lower electrical field of only 6 V/μm, also see Fig. 7 (c). Considering the fact that the composite possesses the same elastic modulus as those of electrotrictive P(VDF-TrFE) polymers, the result demonstrates that this all organic composite approach can result in a 10 times reduction of the applied field. The composite properties such as the breakdown field and dielectric constant can be improved and as a result, much higher strain level with low applied field can be expected in this new class of polymer-like material.

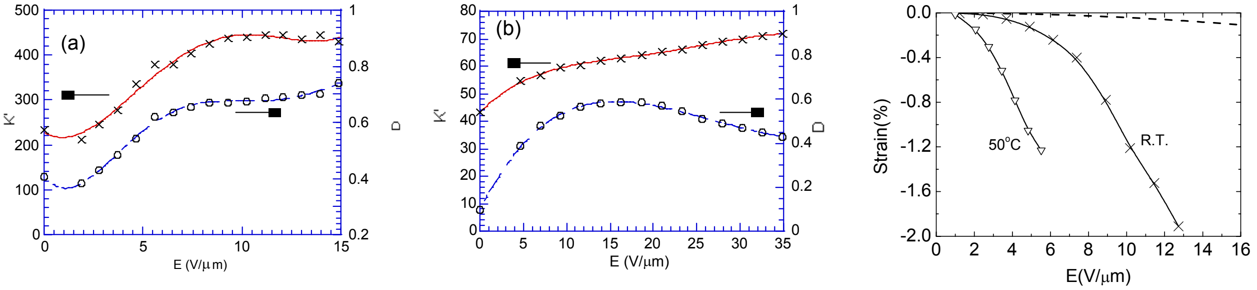

Figure 7. (a) Dielectric properties of the all-organic composites. The real part of the dielectric constant (K') and dielectric loss (D) as a function of the applied field amplitude for the composite with 40wt% CuPc and (b) Dielectric properties the polymer matrix as a function of the applied field amplitude. (c) The strain amplitude as a function of the applied field amplitude measured at room temperature and 50°C. For the comparison, the strain from the electrostrictive P(VDF-TrFE) copolymer at the same field range is also shown (the dashed curve). The applied field is at 1 Hz.

The results of the strain measurement indicate that the field induced strain S is proportional to the square of the applied electric field, suggesting that the strain response originates from either the Maxwell stress (the electrostatic force), or the electrostriction, or both. When a dielectric material is subject to an electric field E, it will experience an electrostatic force (Maxwell stress) due to the Coulomb force between charges. The strain induced by the Maxwell stress along the applied field direction is [24]

$$S = \frac{1}{2} K \varepsilon_0 E^2 (1 + 2 \sigma)/Y \qquad (3)$$

Here we assumed that the dielectric material is isotropic and σ is the Poisson's ratio. The electrostriction is strain generated due to a change in the polarization in a material under constant stress, which is equal to $S = ME^2$, where M is the electrostrictive coefficient and is proportional to the square of the dielectric constant.

From the dielectric and elastic data, the contributions to the strain response from the Maxwell stress and electrostriction may be estimated. Assuming that the composites is homogeneous, the strain due to the Maxwell stress under a field of 13 V/μm is about -0.1%. For the electrostriction from the polymer matrix, assuming that all the applied field is totally loaded on the polymer matrix because its dielectric constant is much lower than that of CuPc, it is also about -0.1%. The measured strain response, therefore, is about one order of magnitude higher than the combined strain from the two.

In an early study on the field induced strain in a polyurethane elastomer, it was observed that a non-uniform electric field distribution can significantly enhance the strain response (more than 5 times in that case) if the strain is proportional to the square of the local field [25]. The composites investigated here are highly heterogeneous where a large variation in the local fields is likely, which will enhance the strain response. In addition, bond length and conformation change in CuPc due to electron motions as well as the CuPc molecular reorientation under external fields may also contribute to the strain response [26]. It is also worthy to point out that CuPc is not the only choice, some other high dielectric constant organic polymers including some conducting polymers may also be used as filler. And the best results will be expected by grafting high dielectric constant polymer to the P(VDF-TrFE) copolymer or terpolymer chains.

V. Conclusions

By making use of the large strain associated molecular conformation change and the large ferroelastic coupling in P(VDF-TrFE) based ferroelectric polymers, a very large electrostrictive strain can be obtained in two defects modified P(VDF-TrFE) polymers, i.e., the P(VDF-TrFE) based terpolymers and high energy electron irradiated copolymers. The functions of the defect structures, introduced via the termonomers in the terpolymer or the high energy electron irradiation in the irradiated copolymers, are (1) to broaden the temperature range in which a polar and non-polar phase can reversibly induced by external fields, (2) to eliminate the nucleation barriers in the transformation between the polar and non-polar phases, and (3) to lower the transformation region to room temperature. As a result, a large electrostrictive strain can be achieved at room temperature over a broad temperature range in these modified polymers.

Compared with the high energy irradiation, the terpolymer approach to modify the copolymer is more attractive since it reduces the manufacture cost and simplifies significantly the processing steps. In addition, it reduces greatly the undesirable side effects introduced by the irradiation to the polymers and hence, can produce a modified polymer with much better electromechanical responses compared with the high energy irradiated copolymers, as has indeed been observed.

In order to reduce the high operation fields required in these polymers which originate from the low dielectric constant in the polymers, we investigated an all organic composite approach in which semiconductor organic solids with very high dielectric constant were used as the fillers and the electrostrictive polymers based on modified P(VDF-TrFE) polymers as the matrix. We showed that this approach could produce a composite (with the filler in the 40 – 60 wt% composition range) with high dielectric constant (>400) and a high induced strain under a low applied field. Furthermore, the new composite exhibits an elastic modulus similar to that of the matrix and is flexible, which are very different from the high dielectric composites developed earlier in which inorganic materials are used as the fillers.

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