Dielectric Switching Studies of Polyvinylidene Fluoride Thin Films with Dominant Planar Ferroelectric Domain Configuration for Flexible Electronic Devices

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ABSTRACT

Electrical switching characteristics of the polymer chains of polyvinylidene fluoride (PVDF) thin films with dominant planar domain configuration were investigated in this work. PVDF a semi-crystalline piezoelectric polymer is known to undergo structural transformation when subjected to electric field. In this study, the I-V characteristics of PVDF was analyzed by varying the delay time from 0.1 to 0.001 seconds in order to understand the response of switching behavior; a promising attribute that governs the operational speed of the device. A hysteretic behavior in the I-V characteristics was observed at different drive voltages. The ferroelectric polarization domains responds at different voltages and give rise to polarization switching currents. In addition to this, at relatively larger voltages (> 10 V) the amorphous intermediate regions of PVDF is expected to undergo an amorphous to crystalline transformation. Hence, the switching characteristics of the ferroelectric domains in the form of switching currents and the dipolar re-orientation arising due to the amorphous to crystalline transformation by rotation of polymer chains are captured at different voltages. Furthermore, a longer delay time (0.1 seconds) is employed to capture the current arising from a reversible amorphous to crystalline transformation. The dielectric relaxation time for the rotation of polymer chains in PVDF was inferred from independent studies and observed to be between 100 to 500 μS.

Index Terms — **thin film, ferroelectric, polyvinylidene fluoride, polarization, capacitance**

1 INTRODUCTION

POLYVINYLIDENE fluoride (PVDF) and its copolymers are one of the most widely used ferroelectric polymers that have been attractive for various applications including sensors, actuators, energy harvesters, biomedical devices and other flexible device applications[1,2]. PVDF a semi-crystalline polymer shows a complex structure that has been extensively studied for flexible piezoelectric device applications. PVDF is known to stabilize in five distinct crystalline phases related to different chain conformations α, β, γ, δ and ε, in which the most investigated phases are α, β, γ [3,4]. The β–phase is known to exhibit piezoelectric properties due to the non-centrosymmetric feature of the crystallization. Dipole moment of two chains containing C-F and C-H in the unit cell adds up resulting in a net dipole moment perpendicular to the carbon

backbone with fluorine acting as negative and hydrogen as positive. Hence, the β phase has the largest spontaneous polarization per unit cell and thus exhibits superior ferroelectric and piezoelectric properties when compared to other phases of PVDF [5,6]. The external electric field has an impact on the structural transitions of PVDF and its co-polymers [7]. X-ray diffraction based electric field studies are one of the widely used methods to look into the effect of such transitions. Poling induced crystallinity, which involves high electric field has been studied earlier [8], and in addition in-situ studies on amorphous to crystalline transformation in the presence of the low electric field with the help of X-ray diffraction has been reported [9]. The external electric field causes rotation and re-orientation of polymer chains that leads to switching of dipole orientation resulting in polarization switching. Das *et al* reported about the relation between switching time and switching voltage with dimensions of PVDF-TrFE(Triflouroethylene) (close to completely crystalline co-polymer) gated FET [2]. Polarization switching time and the overall relaxation time influences the operational time and speed of the device. Earlier studies reported that the switching time of PVDF-TrFE was considered to be ranging in sub-microseconds to nanoseconds [2,10,11]. There have been limited studies on nanoscale polarization imaging and switching in PVDF-TrFE like films by PFM [12]. Sharma et. al., has detailed the orientation of polarization component of PVDF-TrFe based on PFM studies [13]. It has been shown that local switching in PVDF-TrFE can proceed either by 120^0 or 180^0 dipole rotation about the molecular chain depending on the field strength. Hence, the polarization switching and the microscopic origin of their features are of continued interest for fundamental understanding.

In ferroelectric systems, polarization switching is associated with dipolar switching currents. The current flowing through the device provides information about the effective charge density and the apparent built-in voltage, even when the device is operated by varying conditions like temperature, strain, thickness, frequency and voltages [11,12,13]. The orientation of polarization components is one of the important factor in deciding the materials utilization in real time devices. It is known from a study that PVDF films synthesized from varying viscosities through solution casting method exhibits different behavioral pattern of polarization components. To the best of author's knowledge, studies focus on out-of-plane polarization properties like coefficient (d_{33}), switching and devices till date. Hence, it will be interesting to study in-plane polarization based properties. In this work, we have made efforts to understand the dielectric switching behavior of pure PVDF films. Though the semi-crystalline PVDF is known to possess inferior piezoelectric property compared to the almost completely crystalline PVDF-TrFE, PVDF offers flexibility in synthesis and tuning the polarization components based on process conditions and also cost effective material for industry applications.

2   EXPERIMENTAL

Commercially available PVDF (Sigma Aldrich) powders and N-Methyl-2-pyrrolidone (NMP) (Sigma Aldrich) solvent with appropriate weight proportion were mixed in a magnetic stirrer to obtain the solution of PVDF. The solutions were casted to films on metal sheet/glass slide by the conventional doctor Blade technique and further baked. Even though baking temperature is enough to produce β phase, in order to attain higher content of the β phase, the baked thin films were annealed further at 90 ˚C. The occurrence of polarization component of PVDF is highly influenced by the processing condition [9]. In this manuscript we focus on the PVDF films that possess dominant planar components, due to the aimed application of flexible sensing and harvesting energy from planar vibrations and fluid flow.

3   RESULTS AND DISCUSSION

3.1   CRYSTALLINE PHASE IDENTIFICATION

Figure 1a shows the X-ray diffraction pattern of PVDF thin film synthesized from a precursor solution. The peak at 2θ = 20·2° relative to the sum of diffraction from the planes (200) and (110) confirms the dominant presence of β-phase and the shoulder peak at 2θ = 18.5° corresponds to (020) plane indicate the presence of minor amount of γ phase [3,14].

Figure 1b shows the Raman spectra of PVDF thin film. The Raman spectra is dominated by a band at 839 cm^{-1} which confirms the high percentage β-phase for annealed PVDF films [15]. The bands at 812 cm^{-1}, corresponds to γ phase and the peak at 882 cm^{-1} corresponds to the mixed phase of PVDF [16]. Figure 1c shows the FTIR spectra of PVDF film. The peak at 875 cm^{-1} represents the β phase whereas, the peaks at 833 cm^{-1} confirm the presence of γ phase. The presence of peaks at 1067 cm^{-1} indicate mixed phases [17]. It is known that the solution casting method often gives rise to mixed phases, which is also evident from our experimental results.

3.2   PIEZORESPONSE FORCE MICROSCOPY

As mentioned in the experimental section, the PVDF films were found to possess varying ferroelectric polarization components depending on the synthesis conditions. The details of those studies could be found elsewhere [9].   The piezoresponse force microscopy (PFM) studies of PVDF thin film that possessed dominant planar components is presented in Figure 2. The PFM studies include domain imaging, polarization switching and local switching spectroscopic studies of the piezoelectric and ferroelectric materials. The sample is placed between the bottom electrode and the PFM tip. The tip acts as a top electrode during the measurements. Measurements were performed in contact mode to obtain surface response information normal (out-of-plane component) and parallel to the film plane (in-plane component) via the electrostatic forces [18]. The PFM study provides the details of surface morphology, amplitude and phase that are related to topography, piezoelectric coefficient (d_{33}) and the orientations of the polarization field respectively present in the film. By applying a positive or negative dc bias voltage to the tip, 180˚ polarization switching is induced which orients polarization either upward or downward [19]. Figure 2 shows images of pure PVDF. The cropped and
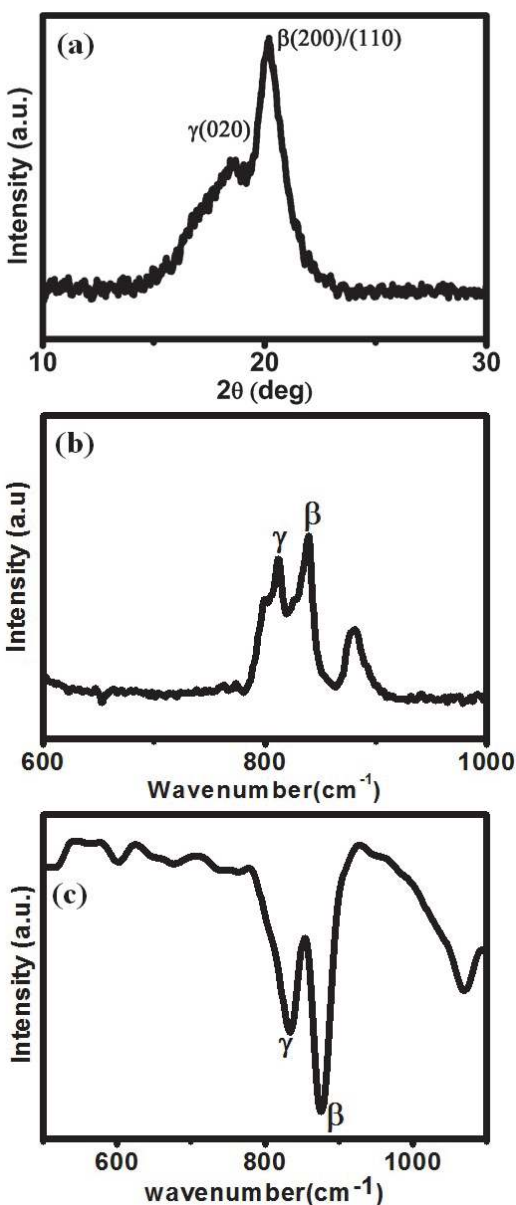
Figure 1. (a) XRD, (b) Raman studies, (c) FTIR of pure PVDF thin film.

numerically magnified contrast in the in-plane phase image of Figure 2f shows that the domains are oriented in opposite direction. Figure 2e shows the distribution of such domain pair present throughout the sample. The extensive studies on piezoresponse imaging and the corresponding theoretical simulation of the same could be found in Ganguly *et al* [9].

The observed in-plane phase contrast are regions with opposite domain orientations either left or right with respect to the probe tip. The domains are out of phase to each other by 180°. Also, the domain separation is observed to be larger (~ 300 - 400 nm) when compared to conventional ferroelectric [9]. It is also known in literature that the crystalline regions of PVDF films are separated by amorphous regions of the same polymer. In this case, the planar domains arrange themselves in Head-to-Head or Tail-to-Tail configurations, where same charges face each other and hence there is a separation by distance, which is decided by the electrostatic energy

minimization. The arrows (Figure 2f) are indicative of a head-to-head configuration of a domain and an opposite representation with 180° rotation (tail-to-tail), is equally plausible. The intermediate region between the domain is assumed to be amorphous in nature which is also capable of storing the charge [20].

Figure 3a displays schematic representation of the domain with the direction of orientation and intermediate amorphous region. The electrical equivalent of such a domain configuration is shown in Figure 3b. Since PVDF exhibits capacitive property, the nanoscale region is also expected to be capacitive in nature. The nature of both the domain can be considered as two capacitor with similar capacitance but oppositely polarized with an amorphous region of specific size (350- 400 nm) that stabilizes such an oppositely oriented domains [9], and in addition the amorphous region in between them is also capable of storing excess charge due to the insulating character of PVDF. It has been reported [9] that the existence of separation between the opposite domains by amorphous region is due to the electrostatic interaction between them. Hence, it becomes important to represent these amorphous regions in equivalent electric circuit.

3.3 CURRENT - VOLTAGE CHARACTERIZATION

To understand the effect of transformation on the electrical property, the I-V characterization was performed for a range of ±20 V on PVDF film. Figure 4a shows the I-V curve of pure PVDF for 0.001 sec delay time. The observed current from these films exhibits hysteresis behaviour. Measurements show that on increasing the voltage the current increases and saturates beyond 7 V. In general, the current is expected to arise from both the dipolar switching/reorientation and the conventional leakage current present in ferroelectric systems. However, in this case the current might be dominated only by the dipolar switching currents. On increasing the field further, the films are expected to undergo a reversible amorphous to crystalline transition (note that such transition is evident above 7 V [9]). On retracing the voltages from 20 V, the reversible transformation from crystalline to amorphous nature associated with the reorientation of polymer chains gives rise to a reduction and change in the direction of the current. However, at 0 V the PVDF films are expected to possess the anti-parallel domain configuration (as observed by PFM) that gives rise to a small change (tending towards zero) in the dipolar switching currents. Similar phenomenon is expected to appear in the negative field direction except for the change in directions. Hence, it gives rise to a hysteretic behaviour in the I-V characteristics, which is dominated by dipolar switching currents and the reorientation of dipolar chains associated with amorphous to crystalline transformation [21]. As we discussed earlier that application of electric field on PVDF samples show its effect on the degree of crystallinity [8]. It was also evident from PFM studies that the PVDF film undergoes a growth in ferroelectric domains under the applied electrical field/voltage, which represents amorphous to crystalline transformation [9,13].
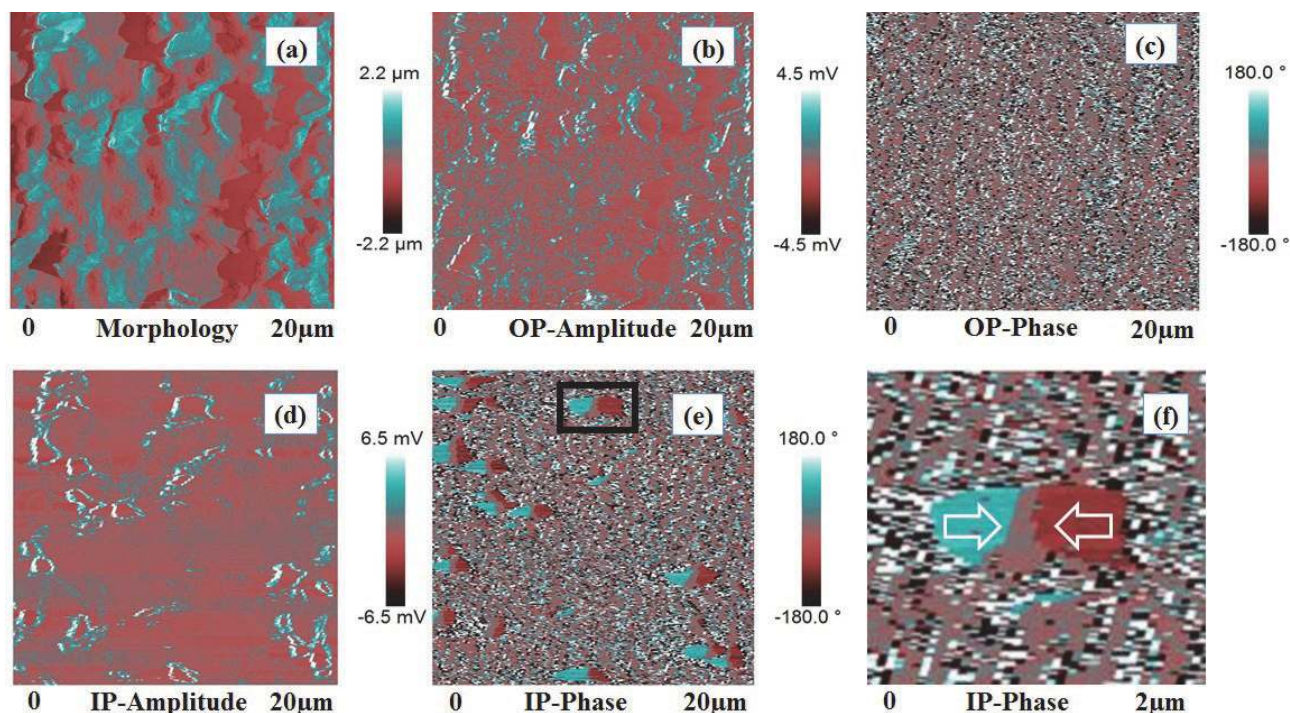
Figure 2. PFM images of pure PVDF film; (a) morphology, (b) out-of-plane (OP) amplitude, (c) out-of-plane phase, (d) in-plane (IP) amplitude, (e) in-plane phase, (f) zoomed region of 2(e) showing the nucleation of opposite orientation domains adjacent to each other..
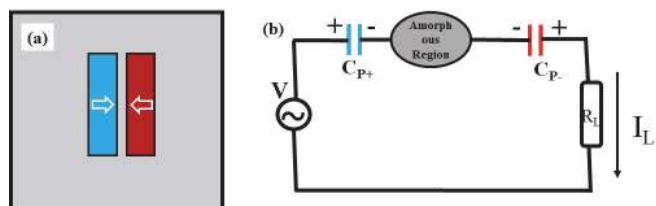

Figure 3. (a) Schematic representation of 2(f) region, (b) electrical equivalent of the schematic.

Figure 4. The in-plane I-V characteristics of pure PVDF at step size; (a) 0.001 sec, (b) 0.01 sec, (c) 0.1 sec. The red arrow indicates the starting point of graph and direction of the black arrows show the sequence in which the measurements were performed.

In order to verify the dominance of dipolar switching current, the measurements were performed by varying the step times. Figure 4b and 4c shows the measurement at larger delay times for PVDF films (i.e. controlling the delay between two data points). When the measurements were performed at step time 0.1 sec or more the hysteretic characteristics disappears and only the current arising from the amorphous to crystalline transformation was observed. The reversibility of the transformation was also evidently observed from the retrace curve. It is worth noting that the contribution from the dipolar switching currents from the domains are quicker than the step times involved in the measurement and hence no change in the currents direction and/or magnitude is observed at 0 V. However, the overall shift of the I-V curves in all the cases could be due to the inbuilt field arising from the charge storage capacity of amorphous regions [20]. The I-V measurements were also performed over a temperature range (not shown) from 25 up to 120°C aiming at the device applications and the stability of the films. A minor and negligible increment in the currents were observed with increase of temperature which is commonly known for materials that involve thermally activated processes as a dominant conduction mechanism [22].
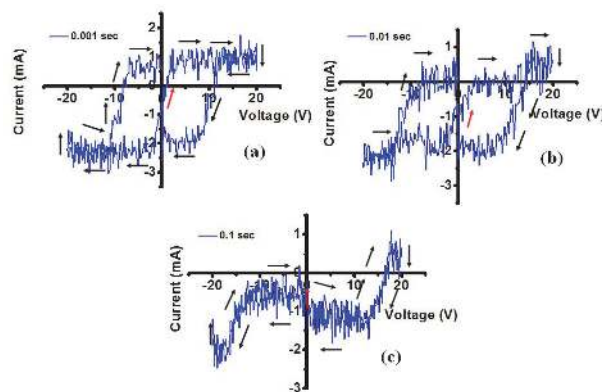
As an independent study from the aforementioned I-V characteristics, the PVDF, thin films were tested for dielectric relaxation in the form of a planar capacitor. The relaxation time of the capacitor plays an important role in determining their switching time. We fabricated a planar sensor whose schematic is shown as an inset in Figure 5b. When tapping forces due to fingerpad in the range of ~ 5 (weak force)-20N (moderate force),[23] was applied over the device between the electrode region, a spike in the piezo current and the consecutive relaxation peak was captured as a response(shown in inset of Figure 5a). It was evident that the device follows the exponential decrement. The discharge voltage of capacitor is given by:

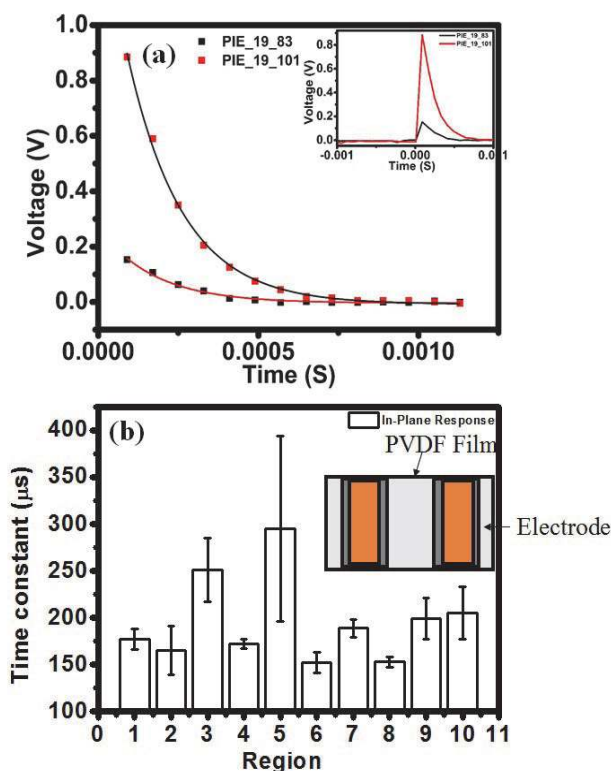$$V(t) = V_o \exp\left(-\frac{t}{\tau}\right) \qquad (1)$$

Figure 5. (a) Fitting of relaxation curve obtain as response of planar device (inset) response of planar device, (b) time constant (τ) at different region between the electrode in the device (inset) Schematic representation of planar device.

where,

τ is RC, time constant,

R is resistance of the PVDF film

C is Capacitance of the PVDF film

V_o is Initial voltage stored in the capacitor

t is Time taken from the beginning of self-discharge

Let us consider that capacitor Cp_+ /Cp_- (see in Figure 3b) with relaxation time τ_P as they are opposite in charge but same in magnitude and the amorphous region has a relaxation time τ_A.

It can be concluded that the collective switching time of the region will be the equivalent relaxation time of capacitor and amorphous region combined. On fitting the exponential curve of response, we observe that it satisfies the capacitance discharge equation.

Figure 5b shows the relaxation time calculated at different regions of the sample between the planar electrodes, it is noticed that time constant τ (relaxation time in this case) lies within the range of 100 to 500 µs. In comparison to earlier studies [10], our results confirm that a collective dipolar relaxations are present in PVDF and operates at a switching time in the range from 100 to 500 µs. Table 1 shows switching time of PVDF reported earlier. It can be observed that switching time reported in the Table 1 are lesser than our reported values. This can be attributed to the dependence of properties on processing conditions and film thicknesses. In most of the studies the co-polymer of PVDF are considered which are far more crystalline than pure PVDF. Our PVDF thin films exhibits mixed phases which influence the crystallinity of the film and in turn the switching time.

Table 1. Reported switching time of various samples.

Sample	Switching Time(Out-of-Plane parallel plate capacitors)	Reference
PVDF	4µs	[24]
PVDF-Trfe	80µs	[25]
PVDF-Trfe	1.5µs	[10]
PVDF-Trfe	120ns	[11]
PVDF-Trfe-Cfe	1.2µs	[10]
PVDF	100-500 µs (In-plane parallel plate capacitor)	Present study

Moreover, reported studies concentrate on Out-of-Plane dipole switching time whereas in our study we report on the switching time of in-plane dipoles. Hence, a range is presented such that the switching time of PVDF films that are prepared with solution casting method irrespective of its thickness might fall within this range. It is also worth noting that these films with dominant planar components would satisfy the need for detecting and energy harvesting planar vibrations (shear forces) when kept in contact with vibrating surfaces.

4 CONCLUSIONS

In this study, we have extensively investigated the macroscopic behaviour of PVDF films which corroborate polarization components and its impact on their electrical properties. Furthermore, we have explored a correlation of I-V characteristics to the switching time which is also confirmed by the device developed from these PVDF samples. The relaxation time is found to be in the range of 100 to 500 µs when analyzed under independent studies. We have studied the influence of amorphous region between the crystalline domain regions on the overall electrical behaviour of the sample. Thus the PVDF with dominant planar response could be utilized under shear strain conditions and would be more efficient than the PVDF films that contains mixed polarization components with out-of-plane orientations.

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