Three different mechanisms of self-discharge behavior in poly(vinylidene fluoride-hexafluoropropylene) for dielectric energy storage

T Band, T Mälzer, S Wickert, H S Leipner, S G Ebbinghaus, K Dörr and M Diestelhorst

Institute of Physics, Martin Luther University Halle-Wittenberg, Von-Danckelmann-Platz 3, 06099 Halle, Germany
Interdisciplinary Center of Materials Science, Martin Luther University Halle-Wittenberg, Heinrich-Damerow-Straße 3, 06099 Halle, Germany
Enspring GmbH, Weinbergweg 23, 06120 Halle, Germany
Institute of Chemistry, Martin Luther University Halle-Wittenberg, Kurt-Mothes-Straße 2, 06099 Halle, Germany

E-mail: tino.band@physik.uni-halle.de

Keywords: ferroelectric polymers, dielectric energy storage, self-discharge behavior, polarization loss, conduction

Abstract

Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) has attracted attention as a matrix material for nanodielectrics, combining the high electrical breakdown of the polymer with the high permittivity of nanoparticles for improved energy storage properties. Although a large number of published works have reported increased discharged energy density for various nanocomposites, polarization and conduction loss mechanisms are rarely investigated. The latter are closely linked to the self-discharge behavior, which is crucial for future applications. This work aims to improve knowledge about loss and self-discharge mechanisms in doctor-blade-coated P(VDF-HFP) since its role in nanodielectrics is not fully understood. Combined analysis of cyclic unipolar electric displacement–electric field (D–E) characteristics and charging–lift–discharging measurements, where the measurement tip is lifted for a specific time between charging and discharging processes, reveals three Debye processes with different relaxation times: 20, 130 and 1340 s. The fast one correlates with the intrinsic conductivity of the polymer, which is dominated by space charge at high electric fields. The other two processes appear to saturate at an electric field of 100 MV m⁻¹ so that their contribution to permittivity drops.

1. Introduction

Dielectric energy storage is essential for fast-developing fields such as power electronics, optoelectronics, DC link capacitors in hybrid electric vehicles, energy harvesting, transistors, and inverters for grid-connected photovoltaics and wind power [1–4]. Recoverable energy density, permittivity, dielectric breakdown strength, cyclability, self-discharge rate and electrical and thermal conductivity are key parameters for dielectric materials. Poly(vinylidene fluoride) (PVDF) and its copolymer are promising candidates to meet these requirements in an optimal way. It is worth noting that investigations on other polymer-based materials also exhibit promising results. Thermally crosslinked divinyltetramethyldisiloxane-bis(benzocyclobutene) with boron nitride nanosheets as a filler, for example, has an excellent temperature stability up to 250 °C [5]. The semi-crystalline poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) possesses a higher energy density than PVDF, making it attractive for dielectric energy storage [6]. However, different chain conformations induce different phases in PVDF, namely, α, β, γ and δ-phases. Li et al. discussed α-, β- and γ-phases with respect to energy storage properties along with their preparation methods [7]. They observed a phase transition from non-ferroelectric α-PVDF to ferroelectric γ-PVDF under electric fields of 200 to 350 MV m⁻¹. Similar results were found by Guan et al in P(VDF-HFP) (96/4 mol%), which contains 4 mol% HFP) [8]. Energy densities of 5 J cm⁻³ and 3.5 J cm⁻³ were observed at 300 MV m⁻¹ for stretched and non-stretched films, respectively. The authors...
found that the alignment of the chain axis was perpendicular to the applied electric field. Thus, the \(-\text{CF}_2-\text{CH}_2-\) dipoles contribute to the overall polarization of the film. Most recent studies concerning dielectric energy storage focus on composite materials to increase energy density due to an increase in breakdown strength or permittivity [9–12].

A rarely studied but crucial area is related to electrical conduction [3] and its influence on self-discharge since conduction could be further enhanced by adding ceramic fillers. Self-discharge is closely linked to internal depolarization processes. Fedosov et al. investigated depolarization mechanisms in corona-charged PVDF via thermally stimulated discharge [13]. They reported Debye relaxation times of 2800 and 31 000 s for dipole polarization and surface-trapped charge, respectively. Observations in polymers using a step voltage to study conduction and polarization mechanisms showed transient currents following the Curie–von Schweidler law instead of a Debye-type exponential law [14, 15]. The steady state in polarization transients is determined by intrinsic conduction. Wang et al. reported a conductivity of the order of \(10^{-10} \text{ S m}^{-1}\) at fields below 200 MV m\(^{-1}\) for P(VDF-HFP) with 15% HFP [16]. Mai et al. studied polarization and depolarization processes in poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) with 30% TrFE [17]. Charge injection starts at high electric fields, so that discharging currents consist of dipole relaxing currents and space-charge relaxation currents. Chen et al. even refer to a limit in dielectric energy storage due to high-field tunneling of charge carriers from the metal electrode into the dielectric film or the escape of carriers from localized states or traps [18]. In general, polymers possess ionic conduction and several electron transport mechanisms like Schottky emission, Fowler–Northem tunneling, Poole–Frenkel hopping and space-charge-limited conduction.

State-of-the-art measurement techniques are based on electric displacement–electric field (\(D–E\)) characteristics at high electric fields, because polarization and loss mechanisms can be characterized simultaneously. However, ferroelectric \(D–E\) characteristics are influenced by ferroelectric switching, dielectric displacement and electric conductivity [19, 20]. The latter is hard to separate out [21]. Consequently, the altered \(D–E\) shape can lead to the misinterpretation of ferroelectric properties [22]. It is rather uncertain how conduction influences the common analysis of energy storage properties obtained from \(D–E\) curves (e.g. column (a) in table 1). The simplest model of a real dielectric consists of a capacitor \(C\) connected in parallel with a resistor \(R\). The capacitor represents a linear dielectric (LD) and the resistor indicates a finite conductivity. Fundamental quantities are summarized in table 1 (see appendix A for a detailed derivation). With this, \(D–E\) curves are calculated and shown in figure 1 by choosing realistic values for permittivity and conductivity of P(VDF-HFP) from Wang et al [16]. The resulting \(D–E\) curve in the third row consists of the following parts: polarization and conduction, which are shown in the first and second rows of the figure, respectively. Unipolar \(D–E\) curves exhibit hysteresis and get pulled along the ordinate when conduction contributes. The discharged energy density \(w_d\) corresponds to the area above the discharge branch in a \(D–E\) diagram and it is common to use this quantity to determine the recoverable energy density of polymers or ceramics. Nevertheless, this area is smaller than the real recoverable energy density of the capacitor as indicated by equation (3(c)) in table 1 and the dashed blue triangle in figure 1(d), which corresponds to \(w_{LD}\) in figure 1(d). Most authors use frequencies in the range of 10 to 100 Hz to reduce conduction loss as equation (4(c)) predicts. Below this frequency range the contribution of conduction (or leakage) current is significant and, consequently, the interpretation of the frequency–dependent quantities is challenging. Apparently, names like stored energy, recoverable energy and energy storage efficiency for \(w_d\), \(w_d\) and \(\eta\), respectively, are misleading as soon as conduction makes a significant contribution. In our example, the conduction is linked to the self-discharge relaxation time which determines the reduction of the stored energy without any connection between the electrodes and is about 1.1 s for P(VDF-HFP) according to equation (6(c)). The free charge carriers \(q\) on the electrodes decay exponentially since Debye relaxation is present \((q = RC \cdot q)\). The relaxation time determines the time when only 36.8% of the initial charge is left on the electrodes, which corresponds to an energy loss of 86.5% due to heat dissipation. Khanchaitit et al. studied poly(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-CTFE)) and introduced an effective
conductivity within $D$–$E$ loops assuming that the difference in polarization at zero field comes mainly from the leakage current [23]. Hence, a separation between ferroelectric and conduction loss was possible. In general, different loss mechanisms in unipolar $D$–$E$ loops can be separated by the shape of the curve. If curves exhibit a gap at zero electric field, as illustrated in figure 1, conduction or an imbalance of polarization and depolarization (e.g. ferroelectric switching) are involved. Both might be separated by cyclic measurements since the imbalance decays over time. Then again, closed $D$–$E$ loops indicate pure polarization losses. To sum up, there is a need to develop an understanding of how conduction influences $D$–$E$ curves as well as their analysis.

This work aims to improve our knowledge about dielectric energy storage mechanisms, especially loss and self-discharge mechanisms, in doctor-blade-coated P(VDF-HFP). One approach is to use cyclic unipolar $D$–$E$ characteristics to study conduction mechanisms. We define an effective conductivity for each cycle observing a Curie–von Schweidler law with steady-state conductivity. Therefore, an effective relaxation time can be obtained which is connected to the self-discharge rate of the polymer. A second approach is made inversely. The self-discharge is directly investigated by means of charging–lift–discharging measurements, where the contact between measurement tip and electrode is interrupted for a specific time between the charging and discharging processes. Based on the self-discharge behavior, we can make a conclusion about the conduction mechanisms. Hence, we investigate self-depolarization effects within the polymer from two perspectives so we are able to separate the influence of polarization, depolarization and conduction mechanisms on the energy storage properties of dielectric materials in detail.

2. Experimental section

2.1. Fabrication and sample preparation

P(VDF-HFP) (94/6 wt%) was purchased from Sigma Aldrich. The pellets were dissolved in dimethylformamide with a solution concentration of 100 g l$^{-1}$ followed by stirring to obtain the polymer dispersion. A 8.5 μm thick film was fabricated on ethanol-cleaned aluminum foil via a solution-casting doctor blade method (figure 2). The temperature of the substrate during deposition was 60 °C. The final film structure was obtained from an in situ drying process using convection and infrared radiation. During this process air heated at 60 °C was flowed above the sample surface with a velocity of 10 m s$^{-1}$ and the sample was irradiated with infrared radiation with a wavelength of around 1620 nm for approximately 20 min. After the substrate was peeled off, sputter deposition was used to metallize the polymer film on both sides with 500 nm thick Al electrodes. The top electrodes for dielectric characterization have a diameter of about 1.1 mm. First, all samples were electrically poled by applying a triangular voltage sweep with an electric field amplitude of 300 MV m$^{-1}$ showing a phase transformation from a non-ferroelectric to a ferroelectric state [8].
2.2. Measurement setup

2.2.1. High-electric-field $D–E$ characteristics

High-electric-field $D–E$ characteristics up to 4 kV were measured under ambient conditions using a modified Sawyer–Tower circuit [24] with a high-voltage amplifier (Trek Model 609E-6). This setup was used to investigate unipolar and bipolar $D–E$ characteristics as well as dielectric breakdown. A voltage ramp of 80 V s$^{-1}$ was applied for the latter. Bipolar $D–E$ loops were examined at 1 Hz to obtain ferroelectric properties. Cyclic unipolar $D–E$ characteristics were used to investigate dielectric energy storage properties at a certain electric field amplitude. Here, a triangular voltage with the same polarity was applied at the top electrode for 30 cycles at 2 Hz. During all high-electric-field measurements the samples were covered with silicone oil to prevent corona discharge.

2.2.2. Charging–lift–discharging measurement

Modified discharging experiments up to 1 kV were performed to obtain the self-discharge rate by using an electrometer (Keithley 6517A) and linear positioners (SmarAct MCS-3C-IDH) to control the contact between the measurement tip and top electrode. First, an electric field was applied for 60 s to completely charge the capacitor. Then, the tip was lifted for a variable but well-defined time (hereafter called the lift time) followed by discharging for 60 s immediately after the tip was brought in contact with the electrode again. Lift times in the range of 10–2000 s were used. Thus, we called this technique charging–lift–discharging (CLD) measurement.

3. Results

3.1. High-electric-field $D–E$ characteristics

3.1.1. Breakdown strength and bipolar $D–E$ characteristics

As a first step the breakdown strength of the polymer film was investigated, resulting in a characteristic strength of 440 MV m$^{-1}$ using two-parameter Weibull analysis [25]. The following measurements were done at electrical fields below 300 MV m$^{-1}$ corresponding to 68% of the characteristic strength to prevent dielectric breakdown of the sample during measurement cycles. Bipolar $D–E$ characteristics present a ferroelectric hysteresis above a coercive field of $(110 \pm 5)$ MV m$^{-1}$ with a remanent polarization of $(23.6 \pm 0.9)$ mC m$^{-2}$ (figure 3(a)). The coercive fields and remanent polarization correspond to the peak positions and the area below the switching peaks in the $j–E$ curve, respectively. The hysteresis splitting $\Delta D$ at zero field does not correspond to the polarization reversal $\Delta P_R$ (double the value of remanent polarization) itself as illustrated in figure 3(b), where the dependence on electric field amplitude is depicted. In the range of 90 to 150 MV m$^{-1}$ the slope of $\Delta D(E_{\text{max}})$ shows a maximum, indicating ferroelectric switching. Afterwards the splitting is still enhanced by increasing the amplitude beyond the coercive field, in contrast to an ideal ferroelectric, due to the contribution of a finite conductivity of P(VDF-HFP) following

$$\Delta D = \Delta P_R + \int_{0}^{(2f)^{-1}} \sigma E \, dt,$$

where $(2f)^{-1}$ is equal to the half-periodic time of the external voltage. Furthermore, no dependence on cyclic measurements was observed except for the initial polarization curve.
3.1.2. Cyclic unipolar D–E characteristics

To suppress the ferroelectric contribution and thus gain more insight into the field-induced conduction mechanisms, cyclic unipolar D–E characteristics were systematically recorded as described in section 2.2.1. Measurement data at 295 MV m\(^{-1}\) are shown in figure 4(a). In contrast to bipolar measurements, a clear dependence on cycle number is revealed.

Di is the value of the displacement field at the amplitude \(E_{\text{max}}\) within the \(i\)th cycle. The slope of the background decreases over time and approaches a constant value as indicated by the red line. The origin of this behavior is an imbalance between polarization and depolarization currents (e.g. ferroelectric switching) with a contribution of electrical conduction through the polymer as discussed in section 1. For a triangular voltage sweep the effective conductivity can be calculated as

\[
\sigma_{\text{eff}}(i) = \frac{2f(D_{i+1} - D_i)}{E_{\text{max}}},
\]

where the obtained value is equal to the conductivity of an ohmic resistance having the same difference \(D_{i+1} - D_i\) within one cycle (see equation (B.2) in appendix B for details). The effective conductivity is proportional to the slope of \(D_i(t)\) and thus to the effective current density. The results for different amplitudes are illustrated in figure 4(b). The effective conductivity drops within the measured range from 19 pS m\(^{-1}\) to 3 pS m\(^{-1}\) and from 30 pS m\(^{-1}\) to 12 pS m\(^{-1}\) for 60 MV m\(^{-1}\) and 295 MV m\(^{-1}\), respectively. The decay of the effective conductivity with cycle number obeys the Curie–von Schweidler law with a steady-state effective conductivity \(\sigma_{\text{ss}}\) following the equation

\[
\sigma_{\text{ss}} = \sigma_0 + \sigma_1 \cdot n^{-n}
\]

with constants \(\sigma_0\) and \(n\). Therefore, the effective conductivity is influenced by conduction currents, polarization and depolarization transient currents. We use non-linear regression to separate the time-dependent and time-independent contributions. The latter is determined by the steady-state conductivity and this steady state is not reached within the measurement time.

The fitting parameters \(\sigma_0\) and \(\sigma_1\) as a function of amplitude exhibit a hysteresis, where ferroelectric switching makes the major contribution (figure 5(a)). Starting at 295 MV m\(^{-1}\) and decreasing the amplitude towards zero, \(\sigma_1\) follows a linear behavior as indicated by the red line. By changing the polarity and applying negative amplitudes from zero to −295 MV m\(^{-1}\) a maximum occurs at around −115 MV m\(^{-1}\), corresponding the coercive field. Again a linear relation is found at the branch of decreasing absolute amplitude. Finally, going back.
to the starting point at 295 MV m\(^{-1}\) the curve again undergoes a maximum in the coercive field, indicating a clear dependence on ferroelectric switching. The fitting parameter \(\sigma_0\) exhibits a similar ferroelectric hysteresis, with small differences. On the one hand, a constant value of about 21 pS m\(^{-1}\) instead of a linear behavior is observed when no ferroelectric switching takes place. On the other hand, the switching peaks are found at slightly higher electric fields (−160 and 150 MV m\(^{-1}\)) so that an additional switching process might occur. Actually, the shape of the switching curves for \(\sigma_s\) and \(\sigma_0\) depends on the total number of cycles, the increment of amplitude between two cyclic measurements and also the starting values for non-linear regression. However, the linear relation for the steady-state conductivity is stable after the switching, indicating an intrinsic conductivity for our samples. The relation between \(\sigma_{\text{eff}}\) and thus \(\sigma_s\), and the current density originating from a conduction mechanism is given by equation (B.6). According to this equation, linear behavior between \(\sigma_s\) and \(E_{\text{max}}\) indicates a quadratic dependence of current density on applied electric field for the underlying steady-state conduction mechanism. Thus, a possible mechanism is space-charge-limited current, indicating charge injection from the electrodes as predicted by the Mott–Gurney law [26].

Calculation of efficiency is, among other things, affected by electric conductivity since \(D–E\) shapes are equally altered, as already discussed. Thus, cyclic measurement also reveals a dependence of efficiency on cycle number (figure 5(b)). The efficiencies obtained from the last cycle are greater than those from the first. In purely formal terms, the reason for this is the decay of effective conductivity with increasing cycle number, as discussed earlier. From a physical point of view, the difference in decay between polarization and depolarization within one cycle also affects the efficiency. However, the curves also include the feature of ferroelectric switching. The peak positions for the first cycle are close to those of \(\sigma_0\). With increasing cycle number the minima shift towards smaller electric fields close to the coercive field. This is not exactly the coercive field, and thus the peak position of \(\sigma_s\), because the steady-state conductivity resulted from non-linear regression and the steady state is not reached after 30 cycles. The efficiency obtained from the 30th cycle is composed almost exclusively of conduction and non-ferroelectric polarization loss. It drops from 0.92 at 30 MV m\(^{-1}\) to 0.85 at 295 MV m\(^{-1}\). Both losses can be approximately separated by subtracting the conduction loss using \(\sigma_s\) via equation (4(c)). The conduction loss increases from 0.5 mJ cm\(^{-3}\) to 0.15 J cm\(^{-3}\) in the range of 60 to 295 MV m\(^{-1}\). This correlates to 3% and 16% of the total loss, respectively. Finally, figure 5 demonstrates how different loss mechanisms in P(VDF-HFP) can be separated by means of cyclic unipolar \(D–E\) characteristics.

Figure 4. Cyclic unipolar \(D–E\) characteristic. (a) Time dependence of displacement and external electric field and (b) effective conductivity at various amplitudes with the Curie–von Schweidler law of P(VDF-HFP).
The results of discharged energy density and related effective permittivity calculated with equations (3)(a) and (2)(b), respectively, are shown in figure 6(a). The mean value for discharged energy of all cycles is presented because only a very slight decay with respect to cycle number (less than 2% within 30 cycles) is found, indicating a stable contribution of conduction and polarization mechanisms, which determines recoverable energy density. The discharged energy density increases up to 5.1 J cm$^{-3}$ at an electric field of 295 MV m$^{-1}$. The conduction losses obtained in the previous paragraph are small compared with this value. Therefore, the approximation of the recoverable energy density with $w_d$ works here. The effective permittivity decreases linearly at electric fields above 90 MV m$^{-1}$. With this and $\sigma_s$ an effective relaxation time can be obtained according to equation (6)(c) providing an approximation of the self-discharge rate. Results are depicted in figure 6(b). The effective relaxation time decreases with increasing amplitude and a value of $-1.55$ is found for the slope in a log–log plot. Above 100 MV m$^{-1}$ the self-discharge rate is of the order of 10 s. Nevertheless, this does not mean that after approximately $5\tau_{eff}$ our capacitor is completely discharged. Because the relaxation time depends on electric field or, more precisely, loss of charge due to self-discharge, the electric field within the dielectric also decreases resulting in a higher relaxation time. This finding suggests that there may be several mechanisms with different relaxation times involved.

### 3.2. Charging–lift–discharging measurement

The displacement is measured as a function of time during all three phases of CLD (figure 7(a)). First, the capacitor is completely charged and the final measured displacement $D_c$ consists of three components

\[ D_c = D_{rev} + D_{irr} + D_{cond}, \]

namely, reversible displacement $D_{rev}$, irreversible displacement $D_{irr}$, and the contribution $D_{cond}$ due to conductivity of the sample. The reversible displacement is linked to polarization mechanisms contributing to the recoverable energy density. The irreversible displacement does not contribute to the energy density due to its long relaxation time after the electric field is removed, for instance ferroelectric switching (ferroelectric phases are effectively screened by accumulated interfacial charge since charging times are sufficient [27]). After charging, the measurement tip is lifted for the lift time to interrupt the circuit. During that time the reversible polarization starts to relax. Thus some free charges will be lost on the electrodes due to an internal self-depolarization process, namely $D_{self}$ which is somehow related to the conductivity. Obviously, that loss is time dependent. Finally, the remaining displacement
is measured by discharging the capacitor. During discharging the self-discharge is almost suppressed due to a low series resistance, \( R_s = 1.19 \, \text{M\Omega} \), in the measurement circuit compared with the isolation resistance of the sample, which is in the terraohm regime. By varying the lift time, the self-discharge behavior of the dielectric can

\[
D_{\text{rem}}(t_{\text{lift}}) = D_{\text{lev}} - D_{\text{self}}(t_{\text{lift}}) \tag{11}
\]
be investigated in a time-resolved fashion. Displacement curves illustrating CLD are depicted in figure 7(b). The slope of the charging curve is time dependent due to transient polarization currents. Nevertheless, the slope of the tail yields an approximation of conductivity with a value of around 9 pS m\(^{-1}\) at 120 MV m\(^{-1}\). A clear self-discharge is observed after lifting the tip, because the remaining displacement (value after 60 s) is smaller than the initial displacement \(D_{rev}\) without lifting the tip. Slow polarization processes with relaxation times beyond the charging and discharging time of 60 s are not taken into account. Nevertheless, the discharging time is sufficient since the capacitor is practically empty and polarization processes contributing to energy storage are relaxed.

The remaining displacement decreases with increasing lift time and the precise dependence for different electric fields is presented as a log–log plot in figure 7(c). The log plot does not exhibit a linear graph, indicating the absence of a simple Debye relaxation. In contrast, a model including three different Debye relaxations is in agreement with the experimental finding, as indicated by the solid lines. The model function is given by

\[
D_{rem}(t_{fin}) = \sum_{i} D_i \exp \left( -\frac{t_{fin}}{\tau_i} \right)
\]

with \(D_{rem}(0) = D_{rev}\). The constants \(\tau_i\) and \(D_i\) are the relaxation time and initially stored charge per area of the single Debye process, respectively. The three different contributions are illustrated by the dashed lines for 10 MV m\(^{-1}\).

Results of non-linear regression indicate that the relaxation times are independent of the electric field within the measured range except for a small scattering below 40 MV m\(^{-1}\) (figure 8(a)). Fast, medium and slow processes with relaxation times of about 20, 130 and 1340 s, respectively, are found. In addition the total time constant \(\tau_0\) is defined as

\[
D_{rem}(\tau_0) = \frac{D_{rev}}{e},
\]

which corresponds to a ‘quasi-Debye’ relaxation time combining all involved mechanisms. A power law with an exponent of \(-0.78\) is found for \(\tau_0\) with respect to \(E_{DC}\). The corresponding \(D_i\) are depicted in figure 8(b). The reversible displacement \(D_{rev}\) as a function of electric field follows a linear behavior with a permittivity of about 23.2. Thus the recoverable energy density of P(VDF-HFP) behaves like a linear dielectric below 120 MV m\(^{-1}\). The charge stored due to the medium and slow processes saturates at electric fields above 80 MV m\(^{-1}\). Values for saturation displacement of about 7.0 mC m\(^{-2}\) and 1.8 mC m\(^{-2}\), respectively, are found. At higher electric fields the major contribution to polarization, and therefore energy storage, is determined by the fast process and

![Figure 8](https://example.com/figure8.png)

Figure 8. Results of CLD measurements: (a) different relaxation times with (b) related displacements \(D_i\) of P(VDF-HFP) (curves for \(\tau_0\) and \(D_{rev}\) are a power and linear law, respectively).
consequently \( \tau_0 \) decreases since the fast process offers the smallest relaxation time. The underlying conductivity is of the order of \( 10^{-12} \) S m\(^{-1} \) which is also found as slope during charging, indicating that the fast process is related to the intrinsic conductivity of P(VDF-HFP).

4. Discussion

Both experiments exhibit consistent and complementary results despite their different nature. The cyclic method reveals one effective relaxation time, whereas four different relaxation times are found during the CLD experiment: three constant Debye relaxation times and one field-dependent total relaxation time. The latter and the effective relaxation time obey a power law with respect to DC field and amplitude, respectively. The derived exponents differ by a factor of two as their origin is different, although absolute values are of the same order of magnitude. So far, the three Debye times have not been confirmed by cyclic measurements. However, our results indicate that the self-discharge correlates with the intrinsic conductivity, which can be obtained from a cyclic experiment within \( D - E \) characteristics. This method is even mandatory to separate polarization and conduction loss within \( D - E \) loops, making it appropriate for studying loss mechanisms in dielectric materials. The steady-state conductivity also offers the possibility to calculate the real recoverable energy density. This becomes significant at lower frequencies as already discussed in section 1. Frequency-dependent results might uncover the three Debye relaxations from CLD measurements.

The permittivity obtained from discharging curves is greater than from \( D - E \) loops as anticipated by equation (3(c)). However, a difference of 8.5 between 23.2 (CLD) and around 14.7 (\( D - E \) curve) for electric fields below 120 MV m\(^{-1} \) could not be attributed to a conduction loss alone since an estimation yields only a difference of less than 0.2 according to equations (3(c)) and (4(c)). The permittivity increases because frequency decreases as the contribution of polarization mechanisms increases. Therefore, our experimental frequency of 2 Hz suppresses relevant polarization mechanisms for dielectric energy storage. Nevertheless, the discharged energy densities at 300 MV m\(^{-1} \) are similar to the values reported by different groups at 10 Hz for solution-cast and stretched [6, 8] or hot-pressed and stretched PVDF-HFP [9], indicating a smaller or equal contribution of conduction in our samples. Efficiencies are difficult to compare since on the one hand a different frequency was used and on the other hand a time dependence exists. Nonetheless, the reported efficiencies coincide with our data showing the first cycle with ferroelectric switching, indicating similar behavior. It should be noted that our data for a virgin curve appear similar but with a minimum at threshold electric field, where a phase transition from non-ferroelectric to ferroelectric phase occurs.

It is most likely that only linear polarization mechanisms are present since the reversible displacement is linear below 120 MV m\(^{-1} \) as well. Therefore, the different behaviors of the three Debye processes \( D_1, D_2 \) and \( D_3 \) may originate from different regions inside the polymer. The morphology of semi-crystalline polymers is often described in a two-phase model consisting of crystalline and amorphous phases. This model is not suitable, as our data suggest. Schick et al introduced a model distinguishing between the crystalline, the rigid amorphous and the mobile amorphous fractions [28]. There might also be an interplay from different crystalline phases. However, the fast process becomes dominant at high electric fields and is linked to the intrinsic conductivity. Cyclic measurements reveal a space-charge-limited current regime leading to the assumption that the fast process is determined by the space charge injected from the electrodes into the dielectric at high electric fields. By looking more closely at the difference between the various relaxation times, the self-discharge might be a phased process. The largest amount of charge for the medium (slow) process decays as soon as the fast (medium) process is completely relaxed. Hence, the polarization of one process is somehow stabilized by the next faster one. Optimizing the relaxation time of the fast process may improve the self-discharge behavior of our sample. Further investigations are mandatory to understand the different processes and verify our hypotheses, for instance CLD around the glass transition temperature or varying morphology due to an additional stretching/annealing step. The interface between the polymer and the electrode is also crucial since it influences charge injection.

Finally, in section 1 we estimated a single relaxation time of 1.1 s with values from literature. Our CLD results indicate a relaxation time of 22.8 s as we observed a higher resistivity and permittivity in our film. This relaxation time is related to the intrinsic conductivity and is close to the value obtained for the fast process. Fedosov et al reported two Debye relaxation times for corona-charged PVDF [13]. The longer relaxation related to surface-trapped charges was not observed in our experiment since its contribution to energy storage should be rather low. The reported value of 2800 s for polarization is of the same order of magnitude as the slow process in our sample, but we observe two more Debye relaxations for dipole polarization. This difference might highlight the importance of the interface between polymer and electrode since corona charging demands the existence of only one electrode [29].
5. Conclusions

Thin films of P(VDF-HP) were prepared by doctor blade coating with infrared irradiation and air convection drying. No significant disadvantages besides a lower breakdown strength are observed in comparison with annealed and mechanically strained films with much higher processing times. We employed a rather unusual combination of cyclic D–E loops and charging–lift–discharging measurements to investigate the self-discharge behavior of P(VDF-HFP). Although it is a very crucial topic for dielectric energy storage, investigations referring to this are quite rare. Our investigation revealed three Debye relaxation times in the range of seconds and minutes. By understanding the self-depolarization mechanisms and their connection, it might be possible to optimize the energy storage properties and thus replace biaxially oriented polypropylene as the state-of-art polymer dielectric. Finally, all invented techniques are applicable to different dielectric materials.

Acknowledgments

The authors thank Frank Apsel for fruitful discussions and supporting the film preparation via the doctor blade method.

Appendix A.

In this section we will derive the formulae within table 1, which are used to create figure 1. For a perfect insulating linear dielectric the relation between displacement field \( D \) and electric field \( E \) is given by equation (1(b)). Thus, charged and discharged energy density are equal since branches of the \( D–E \) curve for increasing and decreasing voltage are the same. The resulting energy density \( w_{LD} \) of a linear dielectric is calculated according to equation (3(a)):

\[
 w_{LD} = \int E \, dD_{LD} = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2 .
\]

\( \varepsilon_0 \) and \( \varepsilon_r \) are the vacuum and relative permittivity, respectively. Obviously, the efficiency is 1 for this instance according to (5(a)).

In case of conduction the displacement field is influenced by the shape of the external voltage. In the following, we use a linear electric field sweep which is expressed by

\[
 E(t) = \begin{cases} 
 2E_{\text{max}} t & 0 \leq t \leq (2f)^{-1} \\
 2E_{\text{max}} - 2E_{\text{max}} t & (2f)^{-1} < t \leq f^{-1}
\end{cases}
\]

with time \( t \), maximal electric field \( E_{\text{max}} \) and sweep frequency \( f \). We assume that \( f \ll (R_C)^{-1} \) (\( C \) is the capacity of the sample and \( R \) the series resistance in the circuit) so that the whole electric field is applied at the sample. For reasons of symmetry, we only account for the branch of increasing voltage \( E_c(D) \) when calculating the contribution to the displacement field due to a finite conductivity \( \sigma \) (we omit the subscript ‘c’ in the following):

\[
 D_{\text{cond}} = \int \sigma E \, dt = \frac{\sigma}{2E_{\text{max}} f} \int E \, dE
\]

\[
 = \frac{\sigma}{4E_{\text{max}} f} E^2 .
\]

Note that the conduction is not part of the displacement field from a physical point of view. Nevertheless, we will keep the notation \( D_{\text{cond}} \) in this work for the sake of simplicity. The quadratic dependence of equation (A.4) can be found in figures 1(b) and (e). The red area in figure 1(e) corresponds to the dissipated heat in the resistor and is calculated using equations (2(a)) and (A.4) by

\[
 \frac{1}{2} w_{\text{cond}} = \int_0^{E_{\text{max}}} E \, dD_{\text{cond}} = \frac{\sigma}{6f} E_{\text{max}}^2 ,
\]

whereby the right-hand side is equal to the dissipated heat within a half cycle. The charged energy density of a linear dielectric with conduction loss is indicated by the sum of red and green area in figure 1(f). This area can be derived since the displacement is a superposition of equations (1(b)) and (A.4) as shown below:

\[
 w_c = \int E \, d(D_{LD} + D_{\text{cond}}) = \int E \, dD_{LD} + \int E \, dD_{\text{cond}}
\]
The enclosed red areas in figures 1(e) and (f) have the same size so that
\[ w_1 = w_{\text{cond}}. \tag{A.9} \]

With equations (4(a)), (A.8) and (A.9) the following equation for the discharged energy density of a lossy linear dielectric is obtained:
\[ w_d = w_{\text{LD}} - \frac{1}{2} w_{\text{cond}}. \tag{A.10} \]

Consequently, the discharged energy density is always smaller than the real stored energy on the capacitor since conduction influences the \( D–E \) characteristic. The efficiency may take any value in between \(-1\) and \(+1\) as the following equation shows (\( w_{\text{cond}} \gg w_{\text{LD}} \) or rather \( w_{\text{cond}} \ll w_{\text{LD}} \); both conditions are easily accessible due frequency change):
\[ \eta = \frac{w_{\text{LD}} - \frac{1}{2} w_{\text{cond}}}{w_{\text{LD}} + \frac{1}{2} w_{\text{cond}}}. \tag{A.11} \]

Thus, the interpretation of the ratio of charged and discharged energy density as an efficiency is not ideal. Finally, equation (5(c)) is obtained by substituting equations (A.1) and (A.5) into (A.11):
\[ \eta = 1 - \frac{2}{1 + 3f \tau_{\text{self}}}, \tag{A.12} \]

where \( \tau_{\text{self}} \) is the self-discharge relaxation time of an \( RC \) parallel circuit.

Appendix B.

In appendix A some fundamental relations for energy storage properties were derived. Here, we want to use these relations in a more general way to analyze \( D–E \) characteristics. The gap at zero field (or maximal field) in figure 1(f) correlates with an electric conductivity, as already discussed. A relation between both, gap \( \Delta D \) and conductivity \( \sigma \), is derived below using equation (A.4):
\[ \Delta D = 2 \cdot D_{\text{cond}}(E_{\text{max}}) \tag{B.1} \]
\[ = \frac{\sigma}{2f} E_{\text{max}}. \tag{B.2} \]

The conduction mechanism need not necessarily be ohmic. Therefore, we will call the conductivity in the following 'effective conductivity', which can be field dependent. We derive a relation between current density \( j(E) \), which determines the conduction, and effective conductivity below:
\[ \sigma_{\text{eff}} = \int_0^{f^{-1}} j(t) \, dt \tag{B.3} \]
\[ = \frac{2f}{E_{\text{max}}} \int_0^{f^{-1}} j(t) \, dt \tag{B.4} \]
\[ = \frac{2f}{E_{\text{max}}} \left( \int_0^{(2f)^{-1}} j(t) \, dt + \int_{(2f)^{-1}}^{f^{-1}} j(t) \, dt \right). \tag{B.5} \]

The final relation is obtained by substituting \( dt \) by \( dE \) according to equation (A.2):
\[ \sigma_{\text{eff}} = \frac{2}{E_{\text{max}}} \int_0^{E_{\text{max}}} j(E) \, dE. \tag{B.6} \]

ORCID iDs

T Band @ https://orcid.org/0000-0002-6693-1065

References

[1] Zhu L and Wang Q 2012 Macromolecules 45 2937
[2] Hao X 2013 J. Adv. Dielectr. 3 1330001
[3] Chen Q, Shen Y, Zhang S and Zhang Q M 2015 Annu. Rev. Mater. Res. 45 433
[4] Thakur V K and Gupta R K 2016 Chem. Rev. 116 4260
[5] Li Q et al 2015 Nature 523 576
[6] Xia W, Zhou Z, Liu Y, Wang Q and Zhang Z 2018 J. Appl. Polym. Sci. 135 46306
[7] Li W, Meng Q, Zheng Y, Zhang Z, Xia W and Xu Z 2010 Appl. Phys. Lett. 96 192905
[8] Guan F, Pan J, Wang J, Wang Q and Zhu L 2009 Macromolecules 43 384
[9] Tomer V, Manias E and Randall C A 2011 J. Appl. Phys. 110 044107
[10] Ehrhardt C, Fettkenhauer C, Glenneberg J, Münchgesang W, Leipner H S, Diestelhorst M, Lemm S, Beige H and Ebbinghaus S G 2014 J. Mater. Chem. A 2 2266
[11] Rahimabad M, Mirshekarloo M S, Yao K and Lu L 2013 Phys. Chem. Chem. Phys. 15 16242
[12] Zhang X, Shen Y, Xu B, Zhang Q, Gu L, Jiang J, Ma J, Lin Y and Nan C W 2016 Adv. Mater. 28 2055
[13] Fedosov S N, Butenko A F and Sergeeva A E 2008 Two components of depolarization currents in PVDF caused by relaxation of homo- and heterocharge Photoelectronics 17 108–112 (http://liber.onu.edu.ua/pdf/17.pdf)
[14] Vanderschueren J and Linkens A 1978 J. Appl. Phys. 49 4195
[15] Jonscher A K 1999 J. Phys. D: Appl. Phys. 32 R57
[16] Wang G, Huang X and Jiang P 2015 ACS Appl. Mater. Interfaces 7 18017
[17] Mai M, Martin B and Kliem H 2013 J. Appl. Phys. 114 054104
[18] Chen Q, Wang Y, Zhou X, Zhang Q and Zhang S 2008 Appl. Phys. Lett. 92 142909
[19] Lines M E and Glass A M 1977 Principles and Applications of Ferroelectrics and Related Materials (Oxford: Clarendon)
[20] Yan H, Inam F, Viola G, Ning H, Zhang H, Jiang Q, Zeng T, Gao Z and Reece M J 2011 J. Adv. Dielectr. 1 107
[21] Meyer R, Waser R, Prume K, Schmitz T and Tiedke S 2005 Appl. Phys. Lett. 86 142907
[22] Scott J F 2007 J. Phys.: Condens. Matter 20 021001
[23] Khanchiapit P, Han K, Gadinski M R, Li Q and Wang Q 2013 Nat. Commun. 4 2845
[24] Rost A 1978 Messung dielektrischer Stoffeigenschaften (Berlin: Akademie-Verlag)
[25] Tomer V and Randall CA 2008 J. Appl. Phys. 104 074106
[26] Mott N F and Gurney R W 1940 Electronic Processes in Ionic Crystals (Oxford: Clarendon)
[27] Fedosov S N and von Seggern H 2004 J. Appl. Phys. 96 2173
[28] Schick C, Wurm A and Mohammed A 2003 Thermochim. Acta 396 119
[29] Giacometti J A and Oliveira O N Jr 1992 IEEE Trans. Electr. Insul. 27 924