

TIME AND POLING HISTORY DEPENDENT ENERGY STORAGE AND DISCHARGE BEHAVIORS IN POLY(VINYLIDENE FLUORIDE-*CO*-HEXAFLUOROPROPYLENE) RANDOM COPOLYMERS*

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Abstract We studied cycle time (0.01–10 s with triangular input waves) and poling history (continuous versus fresh poling) dependent electric energy storage and discharge behaviors in poly(vinylidene fluoride-*co*-hexafluoropropylene) [P(VDF-HFP)] films using the electric displacement — the electric field (*D-E*) hysteresis loop measurements. Since the permanent dipoles in PVDF are orientational in nature, it is generally considered that both charging and discharging processes should be time and poling history dependent. Intriguingly, our experimental results showed that the charging process depended heavily on the cycle time and the prior poling history, and thus the *D-E* hysteresis loops had different shapes accordingly. However, the discharged energy density did not change no matter how the *D-E* loop shape varied due to different measurements. This experimental result could be explained in terms of reversible and irreversible polarizations. The reversible polarization could be charged and discharged fairly quickly (< 5 ms for each process), while the irreversible polarization depended heavily on the poling time and the prior poling history. This study suggests that it is only meaningful to compare the discharged energy density for PVDF and its copolymer films when different cycle times and poling histories are used.

Keywords: P(VDF-HFP) random copolymer; Charging and discharging behaviors; Time and poling history dependence; Dipole switching; Compensation polarization.

INTRODUCTION

Dielectric capacitor films with a high energy density, low losses and a rapid discharge speed are highly desirable for compact and reliable electrical power systems^[1–3]. Due to the low dissipation factor, excellent high frequency response, high dielectric strengths and the self-clearing property, polymer capacitor films are of great importance among all capacitor materials^[4–6]. Unfortunately, no single traditional dielectric polymer alone [*e.g.*, biaxially oriented polypropylene (BOPP), poly(ethylene terephthalate) (PET), or poly(vinylidene fluoride) (PVDF)] so far has been discovered to have both high energy density and extremely low losses. For example, BOPP has a high breakdown strength (> 700 MV/m), inherently low losses, excellent high frequency responses, a low dissipation factor and good self-clearing ability^[7, 8]. These good dielectric properties of BOPP are attributed to its nonpolar hydrocarbon molecular structure. However, this nonpolar structure limits the dielectric response (dielectric constant is only 2.2 for BOPP) and the ultimate energy density (4.88 J/cm³ at 700 MV/m for BOPP) for linear dielectric polymers.

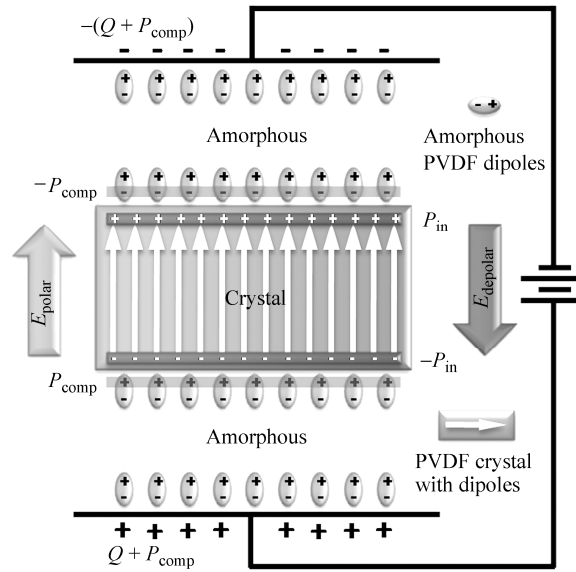
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Scheme 1 Schematic representation of the polarization mechanism for a ferroelectric PVDF crystal sandwiched between two amorphous PVDF layers

In contrast to linear dielectrics, ferroelectric PVDF has a potential to achieve high energy density because of its high dielectric constant (due to a high density of permanent dipoles) and high dc electric breakdown strength^[9–15]. In a previous report on the dipole reorientation mechanism in PVDF and its copolymers^[16], it is indicated that after the dipoles in ferroelectric crystals are aligned by an external electric field (*i.e.*, generating a P_{in}), a compensation polarization (P_{comp}) is induced in the amorphous phase right at the amorphous/crystalline interface (see Scheme 1). The induced compensation polarization plays an important role in the dipole switching behavior during both forward and reverse (or discharge) poling processes. During a forward poling process, the accumulation of compensation polarization is time dependent because the amorphous dipoles are orientational in nature and have a unique relaxation time at a specific temperature and a specific electric field. For example, depending upon the poling electric field, the dipole flipping time decreased from *ca.* 1 ms at 200 MV/m to *ca.* 20 ns at 840 MV/m for a 20 nm thick P(VDF-TrFE) 75/25 thin film^[17]. During the reverse poling or discharge process, the release of the compensation polarization in the amorphous phase depends on the persistence of aligned dipoles in the crystalline phase. In normal ferroelectric polymers, most crystalline dipoles inside the crystals would remain oriented even when the external electric field was removed, because ferroelectric β crystals have a spontaneous polarization. As a result, the release of the compensation polarization will be slow and less than 100%. For example, it could take more than 30 min for the undischarged compensation polarization to completely disappear after a forward poling of a PVDF film at 200 MV/m^[18]. Intrinsically, conventional ferroelectric polymers are designed by the Nature as excellent switches for transducers^[19] and nonvolatile memories^[20, 21], rather than electric energy storage devices such as dielectric capacitors^[1, 22].

However, novel modified ferroelectric polymers still hold the hope for the electric energy storage application. In principle, when an external field is applied, both crystalline and amorphous dipoles in PVDF will be oriented and a significant amount of electric energy density is stored by this poling process (see Scheme 1). This part of stored energy density will be completely released when the oriented dipoles quickly switch back to a random (or antiferroelectric-like) state with a zero net dipole as the electric field decreases to zero during the discharge process. Therefore, new strategies such as relaxor-like ferroelectrics^[23–26] have been actively pursued. For example, PVDF is modified with bulky comonomers such as chlorotrifluoroethylene (CTFE) and hexafluoropropylene (HFP) to break up large crystals. The corresponding P(VDF-CTFE) and P(VDF-HFP)

random copolymers exhibit relaxor-like ferroelectric behavior and have achieved an energy density as high as 17–25 J/cm³ at *ca.* 600 MV/m for millisecond discharge^[22, 27]. Unfortunately, the dielectric loss ($\tan\delta$) is > 0.02 at 1 kHz at the ambient temperature and the ferroelectric loss is as high as 40%–60% in P(VDF-CTFE) and P(VDF-HFP) films, indicating that a significant amount of oriented dipoles still does not switch back to the random state during discharging^[16, 27–29]. Furthermore, this ferroelectric loss is also discharge time dependent; an additional 40% loss in discharged energy density when the discharge time decreases from 1 ms to 1 μ s^[27]. As such, more fundamental studies are required to understand the charging and discharging behaviors and solve the slow and less than 100% discharge problem for modified PVDF copolymers.

Because of the orientational nature of the dipoles in PVDF, a general belief is that both charging and discharging processes should be time and poling history dependent. In this work, we observed that the charging process was poling time and poling history dependent while the discharge was nearly independent of the discharge time (in a range of 0.005–5 s) and the prior poling history. To explain these experimental results, we propose that there should be reversible (fast) and irreversible (slow) orientational polarizations in the sample. On the basis of this study, we intend to provide suggestions on how to achieve highly reversible polarization in PVDF-based ferroelectric polymers.

EXPERIMENTAL

Materials

P(VDF-HFP) 96/4 resin (pellets) was purchased from Aldrich. Its number-average molecular weight was 1.3×10^5 g/mol and its weight-average molecular weight was 4.0×10^5 g/mol. Using fluorine nuclear magnetic resonance (¹⁹F-NMR), the HFP content was determined as 4.0 mol%.

Film Fabrication and Processing

Film HP with a thickness around 80–100 μ m was prepared by hot-pressing the P(VDF-HFP) 96/4 resin at 240°C followed by immediate quenching into ice/water. Film HP was uniaxially stretched at 12.7 mm/min to an extension ratio of *ca.* 500% at 90°C and 130°C, respectively. The final film thicknesses were *ca.* 20 μ m, and the films are denoted as HPStr90 and HPStr130, respectively. Details for the processing and characterization methods can be found in a previous report^[16].

Instrumentation and Characterization

The electric displacement-electric field (D - E) loops at room temperature were collected using a modified Sawyer-Tower circuit and a triangle unipolar high voltage input^[27]. Gold electrodes were sputtered onto both surfaces of the film with a thickness around 50 nm. The gold electrode area was *ca.* 0.0531 cm² for the D - E loop measurements.

RESULTS AND DISCUSSION

The time dependence of electric energy storage and discharge processes was studied by D - E hysteresis loop measurements with a triangular high voltage input at different cycle times (0.01, 0.1, 1 and 10 s). In addition, the effect of polymorphism on the time dependence was studied by using two P(VDF-HFP) films with the same crystal orientation, similar crystallite sizes, but different α and β crystal contents^[16]. Results of polymorphism and crystallite sizes in films HPStr90 and HPStr130 (films B and C in Ref. [16]) were taken from the previous report and are presented in Table 1. From this table, film HPStr90 had a higher β crystal content and thus would induce a higher compensation polarization at the amorphous/crystalline interface than film HPStr130^[16].

Table 1. α and β contents and estimated average crystallite sizes for α and β PVDF crystals ^a

Films	Crystallinity (wt%) ^b	T_m (°C) ^b	α (wt%) ^c	β (wt%) ^c	$D_{(110)\alpha}$ (nm)	$D_{(110/200)\beta}$ (nm)
HPStr90	32.2	143	18.2	30.6	13.7	11.4
HPStr130	35.6	133	32.9	7.3	19.0	15.5

^a The results in this table are taken from a previous report^[16];

^b Determined by differential scanning calorimetry (DSC);

^c Determined by 1D wide-angle X-ray diffraction (WAXD) using peak-fitting and the Scherrer equation

Figure 1 shows the unipolar D - E loops for film HPStr90 at different poling fields during consecutive poling processes. Namely, at each electric field the same sample was poled four times consecutively with the cycle time being 0.01, 0.1, 1, and 10 s. For the same sample, three electric fields were used; 100, 150, and 300 MV/m. The interval between two consecutive D - E loop measurements was 2 min. At a low poling field of 100 MV/m (Fig. 1a), the shape of D - E hysteresis loops changed from slim and nearly linear at 0.01 s cycle time to very broad and non-linear at 10 s cycle time. The opening-up of the D - E loop at a longer cycle time (*i.e.*, 10 s) indicated that more dipoles were oriented by the electric field in both the crystalline and amorphous phases, resulting in a higher maximum electric displacement ($D_{\max}$). Meanwhile, more oriented dipoles in PVDF crystals prevented the dipole reversal in the amorphous phase during discharge, resulted in a higher remnant electric displacement (D_{rem}). Note that the remnant polarization (P_{rem}) is the same as the D_{rem} because the electric field is zero. Judging from the changes in the D - E loop shape at different cycle times, the complete dipole orientation upon applying an external field should occur beyond the cycle time of 1 s because the D - E loop shape did not change much until after the 1 s cycle time. At a medium poling field of 150 MV/m (Fig. 1b), the driving force for dipole orientation became higher, and similar opening-up of D - E loops was observed with increasing the cycle time. However, the D - E loop shape already substantially changed at the 0.1 s cycle time, indicating that the complete dipole orientation should occur beyond the 0.01 s cycle time. At a high electric field of 300 MV/m (Fig. 1c), the driving force for dipole orientation became even higher. The D - E loop had already opened up even

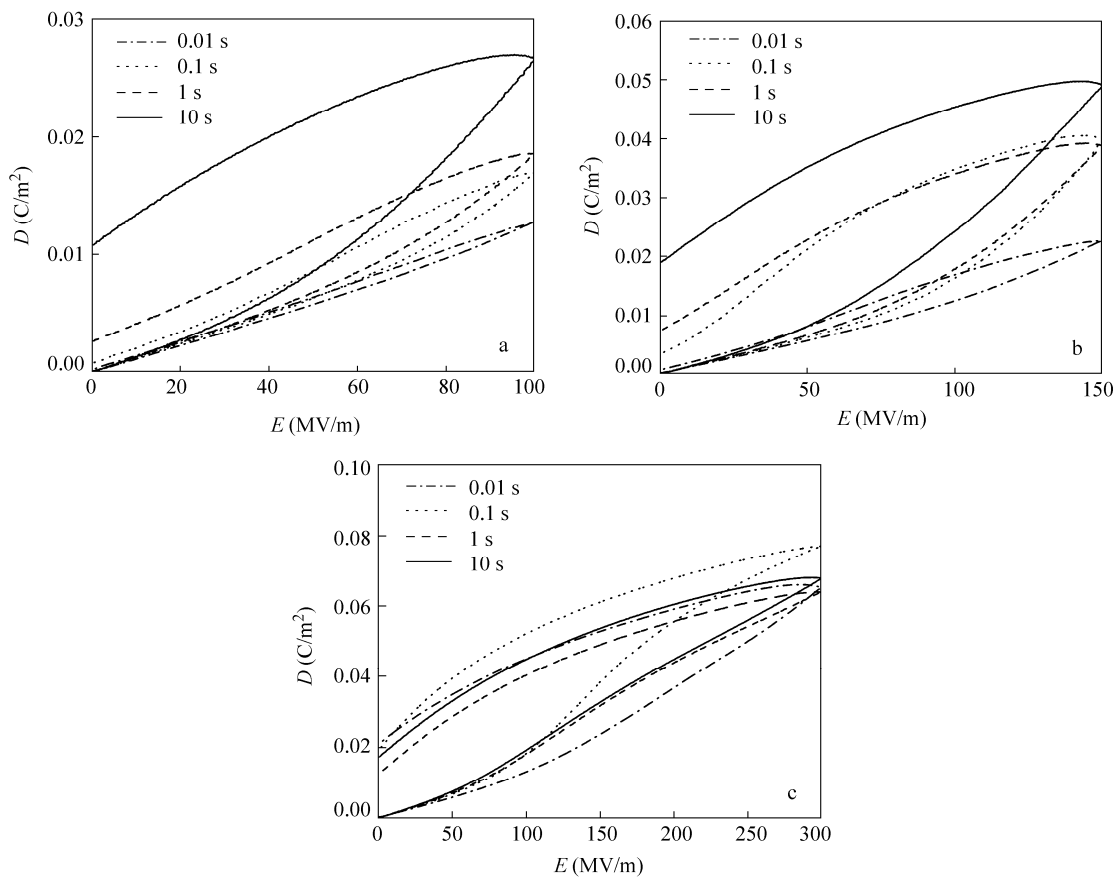


Fig. 1 Unipolar D - E loops for film HPStr90 at various cycle times when the forward poling field is (a) 100, (b) 150 and (c) 300 MV/m, respectively. All the D - E loops are obtained by consecutive poling of the same film with a time interval between the neighboring cycles of 2 min.

at 0.01 s cycle time and the $D_{\max}$ and D_{rem} did not change much with further increasing the cycle time. Obviously, the D - E hysteresis loops were cycle time (or frequency) dependent for P(VDF-HFP) films.

Similar D - E loop measurements were performed for film HPStr130, and results are shown in Fig. 2. Similar trends were seen, namely, with increasing the poling field the D - E loops opened up at a shorter cycle time. Finally, at 300 MV/m the loops already opened up at 0.01 s cycle time. Quantitative comparison of the $D_{\max}$ and D_{rem} for films HPStr90 and HPStr130 is shown in Fig. 3. Figure 3(a) shows the $D_{\max}$ as a function of the cycle time. Obviously, the $D_{\max}$ increased with increasing the cycle time at ≤ 150 MV/m and remained nearly constant for 300 MV/m. Since there was a less β crystal content (7.3 wt%) in film HPStr130 than in film HPStr90 (30.6 wt%), the complete dipole switching time for film HPStr130 was longer. For example, the complete dipole switching times were > 1 s, > 1 s, and < 0.01 s for the poling fields of 100, 150, and 300 MV/m, respectively. Meanwhile, the $D_{\max}$ for film HPStr90 was always higher than that for film HPStr130 at the same poling field and the same cycle time, which again could be attributed to a higher β crystal content in film HPStr90^[16]. The D_{rem} values, which represent the undischarged part of the $D_{\max}$, are shown in Fig. 3(b) for films HPStr90 and HPStr130. At 100 and 150 MV/m, the undischarged part increased with increasing the cycle time, while it was nearly constant at 300 MV/m.

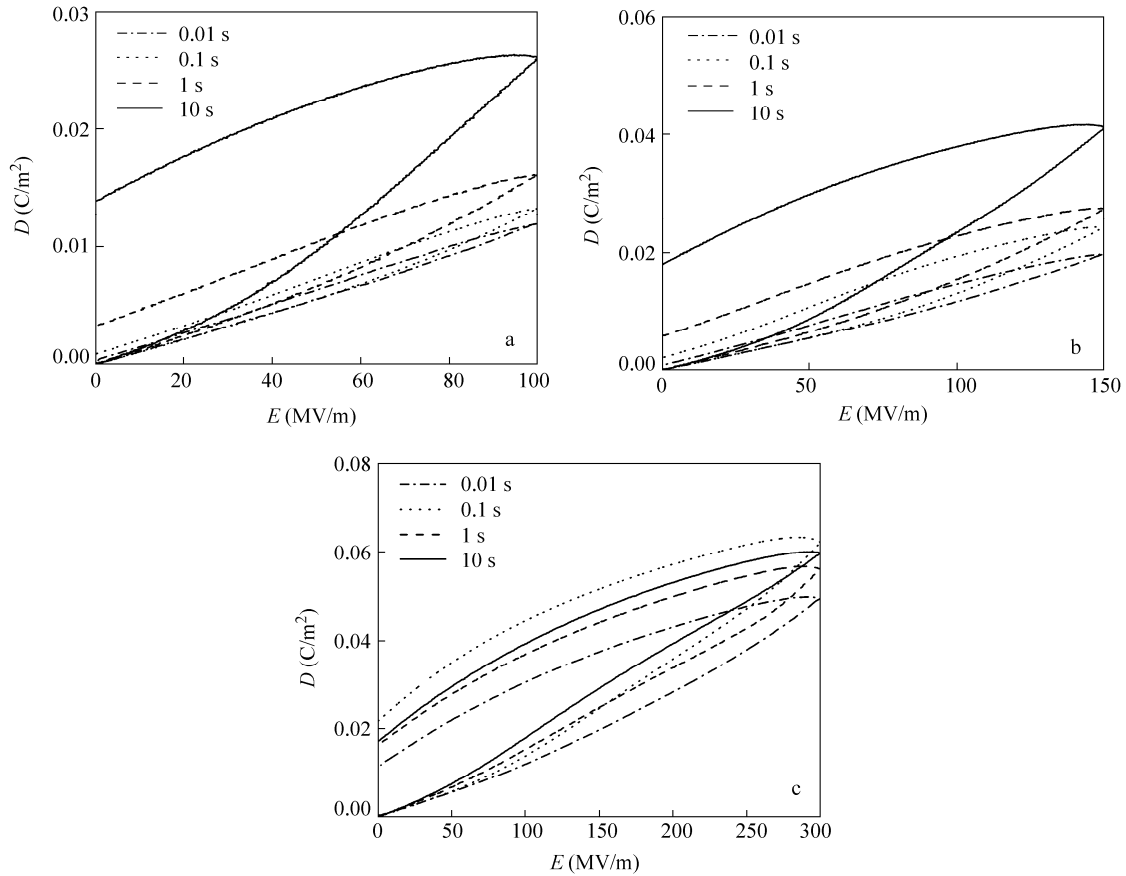


Fig. 2 Unipolar D - E loops for film HPStr130 at various cycle times when the forward poling field is (a) 100, (b) 150, and (c) 300 MV/m, respectively

All the D - E loops are obtained by consecutive poling of the same film with a time interval between the neighboring cycles of 2 min.

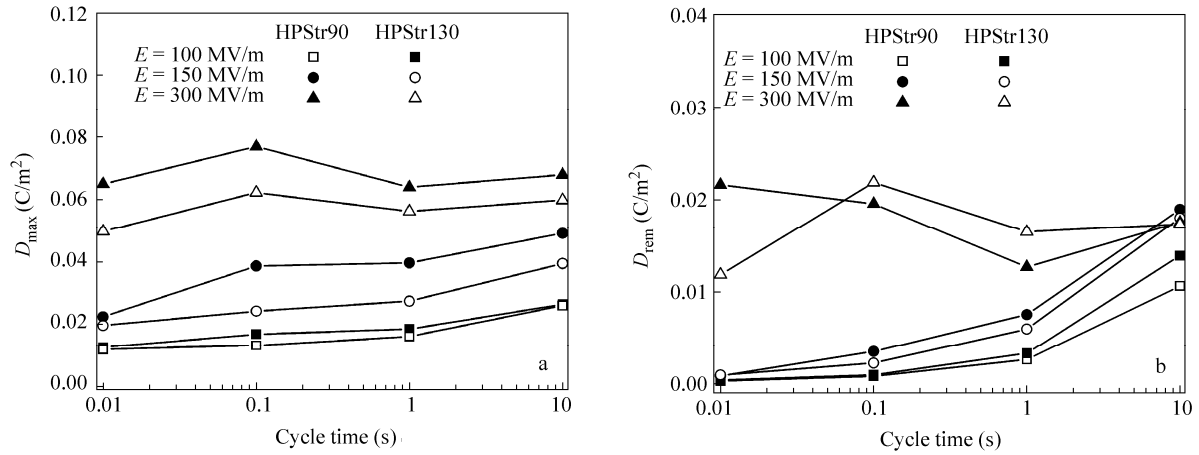


Fig. 3 (a) $D_{\max}$ and (b) D_{rem} as a function of the cycle time for films HPStr90 and HPStr130, respectively

The charged energy density ($U_{\text{e, ch}}$) was directly obtained by integration from the D - E loops ($U_{\text{e}} = \int E dD$) in Figs. 1 and 2. The $U_{\text{e, ch}}$ values as a function of the electric field at different cycle times are shown in Figs. 4(a)–4(d), and are compared between films HPStr90 and HPStr130. First, the $U_{\text{e, ch}}$ for film HPStr90 was generally higher than that for film HPStr130 at various cycle times. Again, this could be attributed to the polymorphism effect^[16]. Second, the $U_{\text{e, ch}}$ increased with increasing the electric field. However, it did not obey the simple $U_{\text{e}} \propto E^2$ rule, but had a shoulder peak between 200 and 350 MV/m. This was typical for non-linear ferroelectric materials and the shoulder peak could be attributed to a fast accumulation of induced compensation polarization due to the orientational transition of crystalline dipoles between 200 and 350 MV/m. Third, for film HPStr90 shoulder peaks always appeared at a lower poling field than that for film HPStr130, suggesting that film HPStr90 was easier to be poled than film HPStr130 because of a higher β crystal content. Fourth, with increasing the cycle time the shoulder peak field gradually decreased. This is clearly shown in Figs. 4(e) and 4(f) for films HPStr90 and HPStr130, respectively, and is consistent with the above results that dipole switching became easier at a longer cycle time because dipole orientation was poling time dependent.

Compared with the charged energy density in Fig. 4, the discharged energy density shows different electric field and poling time dependence as shown in Fig. 5. First, the discharged energy density was significantly lower than the charged energy density. Second, from Figs. 5(a)–5(d), film HPStr90 discharged more energy density than HPStr130. This again could be attributed to the polymorphism effect that more β crystals discharged more energy density, given that the crystallite sizes were small and similar for films HPStr90 and HPStr130^[16]. Third, intriguingly, the discharged energy densities were nearly the same for the same film despite of different cycle times ranging three orders of magnitude from 0.01 s to 10 s, different $D_{\max}$ and charged energy densities as in Figs. 3 and 4.

The percentage of the undischarged energy density is defined as $100(1 - U_{\text{e, dis}}/U_{\text{e, ch}})$, which includes both ferroelectric and conduction losses^[27, 30]. Figures 6(a)–6(d) show the undischarged (%) as a function of the electric field when the cycle time are 0.01, 0.1, 1 and 10 s, respectively. Every curve showed a maximum (see the arrows) between 100 MV/m and 350 MV/m, after which the undischarged (%) decreased and leveled off above 400 MV/m. When the cycle time was the same, the maximum appeared at a lower electric field for film HPStr90 than for film HPStr130, because the higher β crystal content in film HPStr90 caused an easier dipole orientation. The effect of different cycle times on the undischarged (%) is shown in Figs. 6(e) and 6(f) for films HPStr90 and HPStr130, respectively. Clearly, the maximum appeared at a lower electric field at a longer cycle time than at a shorter cycle time. Correlating the undischarged (%) results in Fig. 6 with the charged energy density in Fig. 4 and discharged energy density in Fig. 5, the maximum peaks in the undischarged (%) were caused by the shoulder peaks in the charged energy density rather than the discharged energy density as a function of the electric field. Therefore, the undischarged (%) was also poling time dependent.

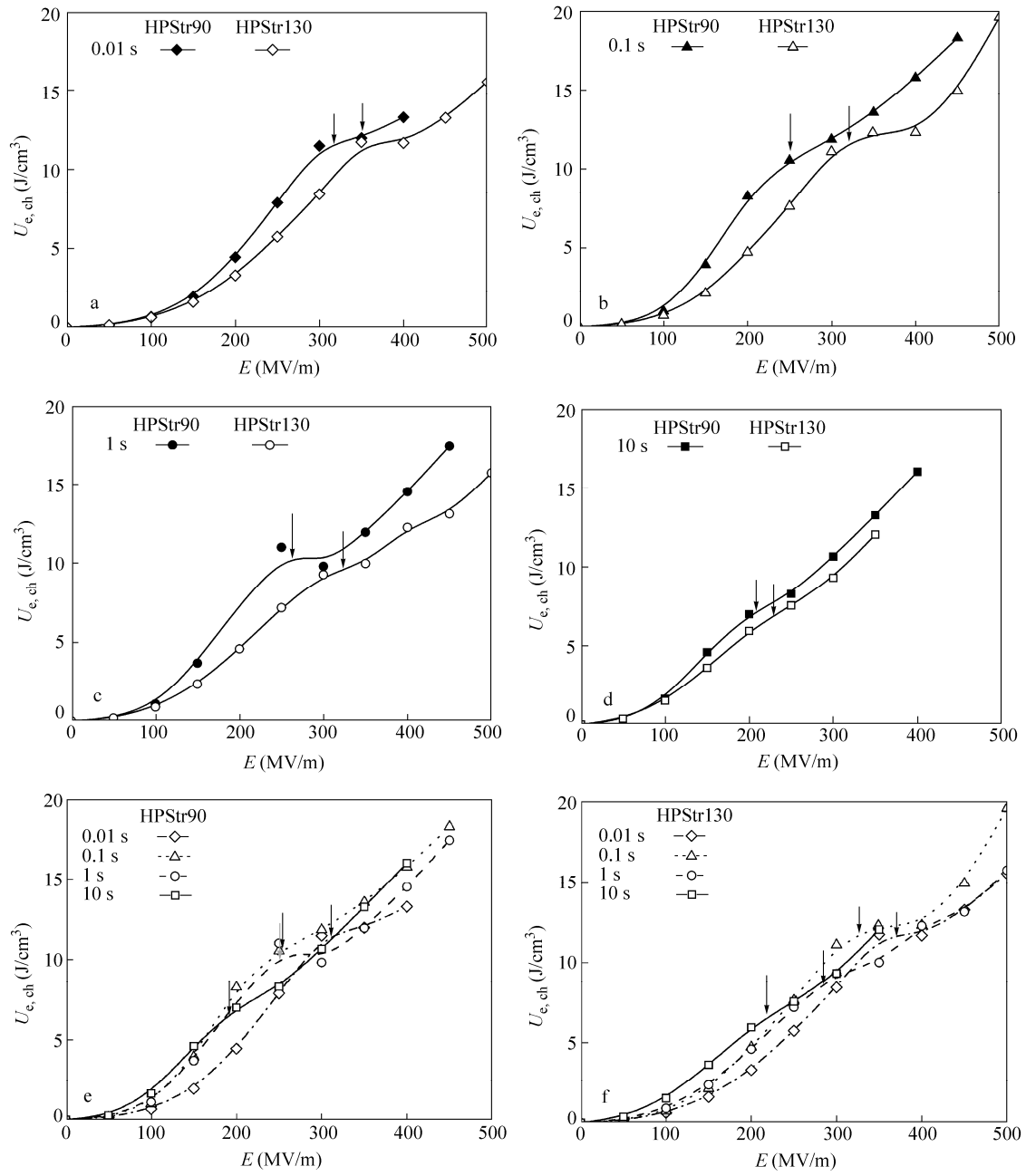


Fig. 4 The charged energy density ($U_{e, ch}$) as a function of the electric field for films HPStr90 and HPStr130 at different cycle times: (a) 0.01 s, (b) 0.1 s, (c) 1 s and (d) 10 s, and the $U_{e, ch}$ as a function of the electric field at various cycle times for (e) HPStr90 and (f) HPStr130

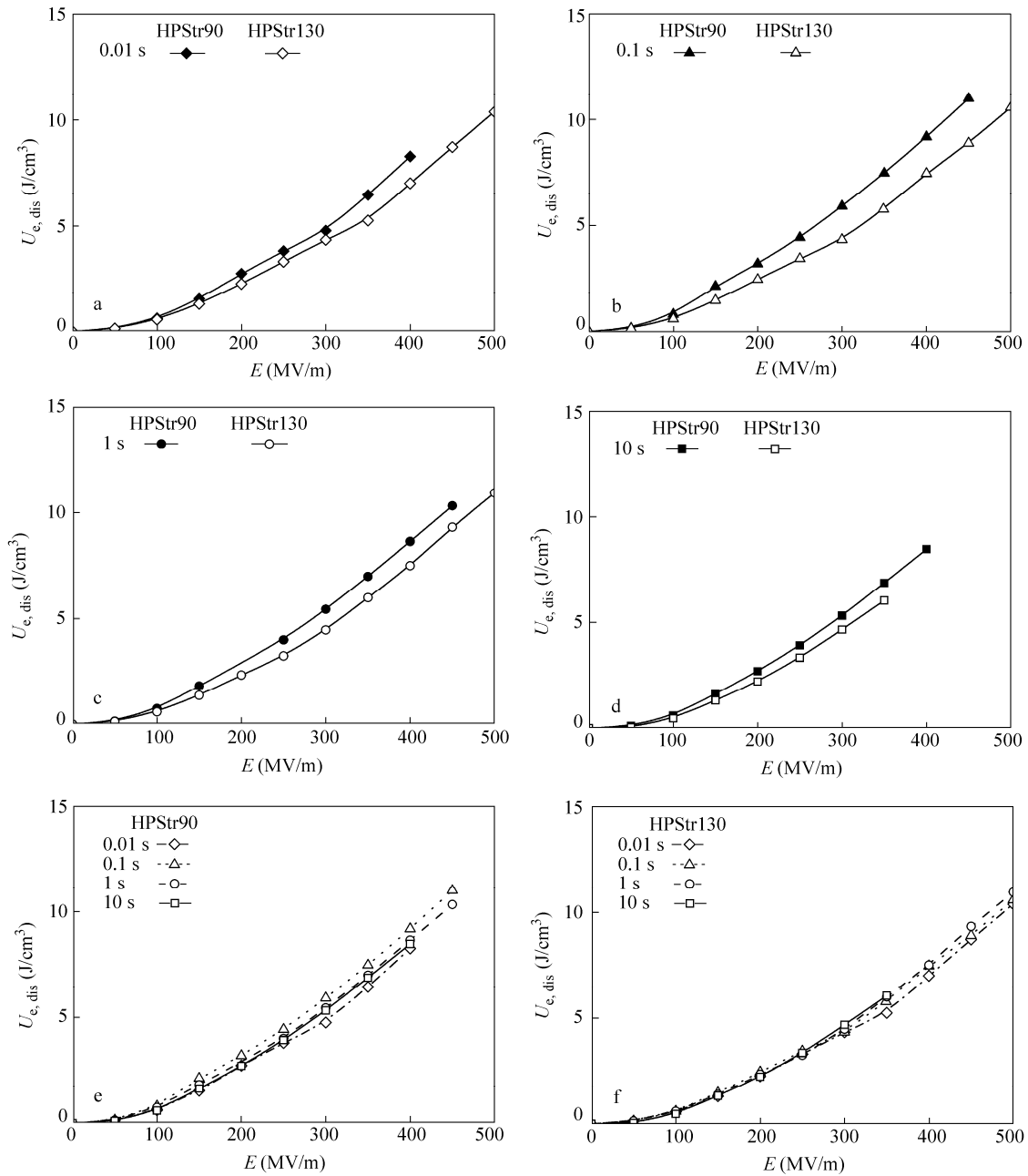


Fig. 5 The discharged energy density ($U_{e,dis}$) as a function of the electric field for films HPStr90 and HPStr130, respectively, with different cycle times: (a) 0.01 s, (b) 0.1 s, (c) 1 s and (d) 10 s, and the $U_{e,dis}$ as a function of the electric field at various cycle times for (e) HPStr90 and (f) HPStr130

In addition to cycling time effect, we also studied poling history effect, as shown in Fig. 7. In previous studies, the D - E loop measurements were performed on the same sample consecutively with an interval around 2 min. Therefore, the later D - E loop had a poling history from the prior D - E loop measurement. In Fig. 7, we performed D - E loop measurements for HPStr90 with a fresh sample every loop. As such, each sample had no prior poling history. Comparing Fig. 7 with Fig. 1, one can see that poling history had significant effect on the shape of D - E loops. For example, at 100 MV/m the D - E loops without prior poling history were still narrow and linear for 0.1 s and 1 s cycle times (Fig. 7), while they were more opened up for film HPStr90 with prior poling

history (Fig. 1). At 150 MV/m the D - E loops without prior poling history gradually opened up with increasing the cycle time (Fig. 7), while they suddenly opened up for film HPStr90 with prior poling history at the 0.1 s cycle time (Fig. 1). At 300 MV/m, the $D_{\max}$ was highest at the 0.1 s cycle time for film HPStr90 with prior poling history (Fig. 1), while the $D_{\max}$ gradually increased with increasing the cycle time for film HPStr90 without prior poling history (Fig. 7).

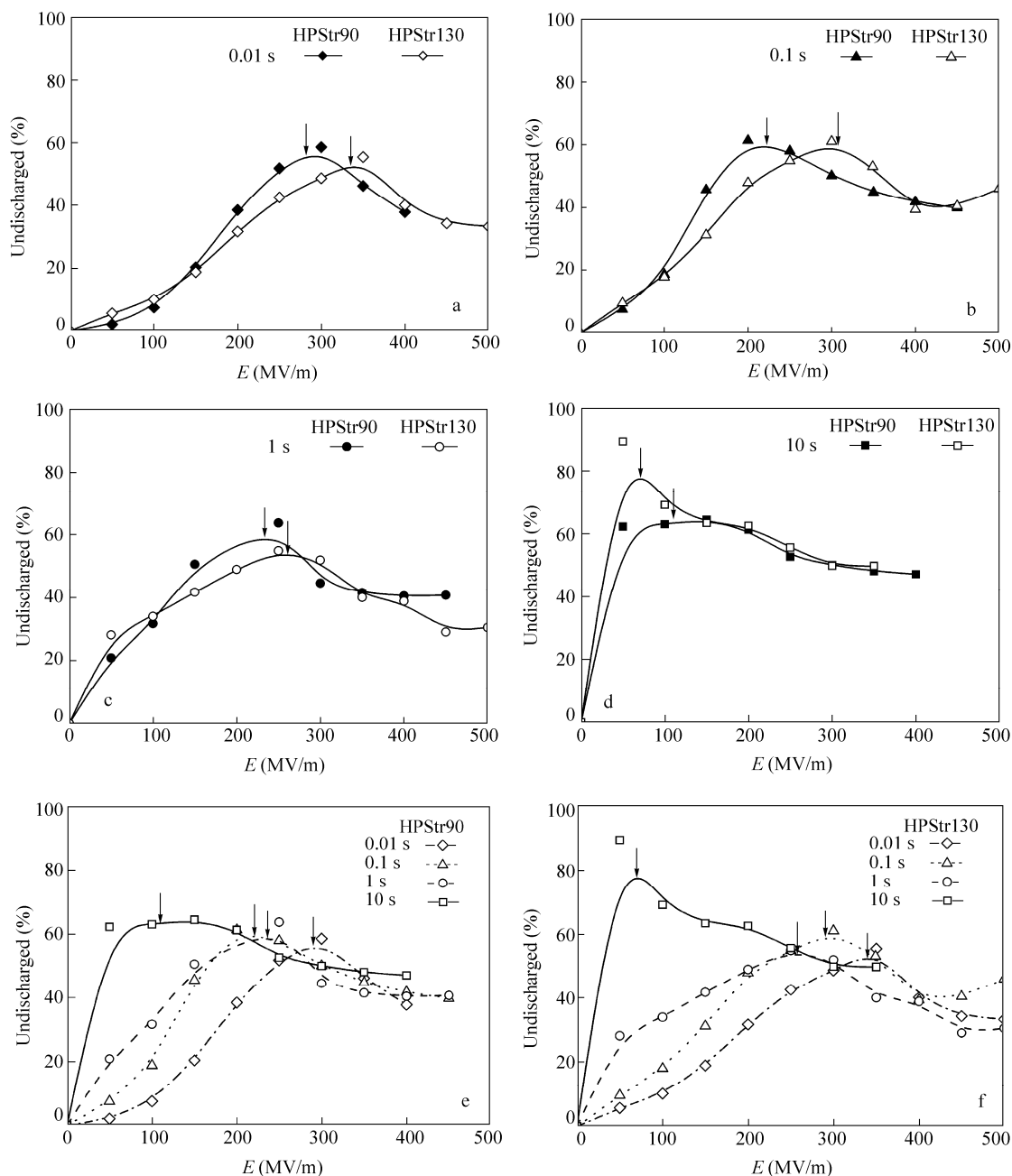


Fig. 6 The undischarged (%) as a function of the electric field for films HPStr90 and HPStr130 with different cycle times

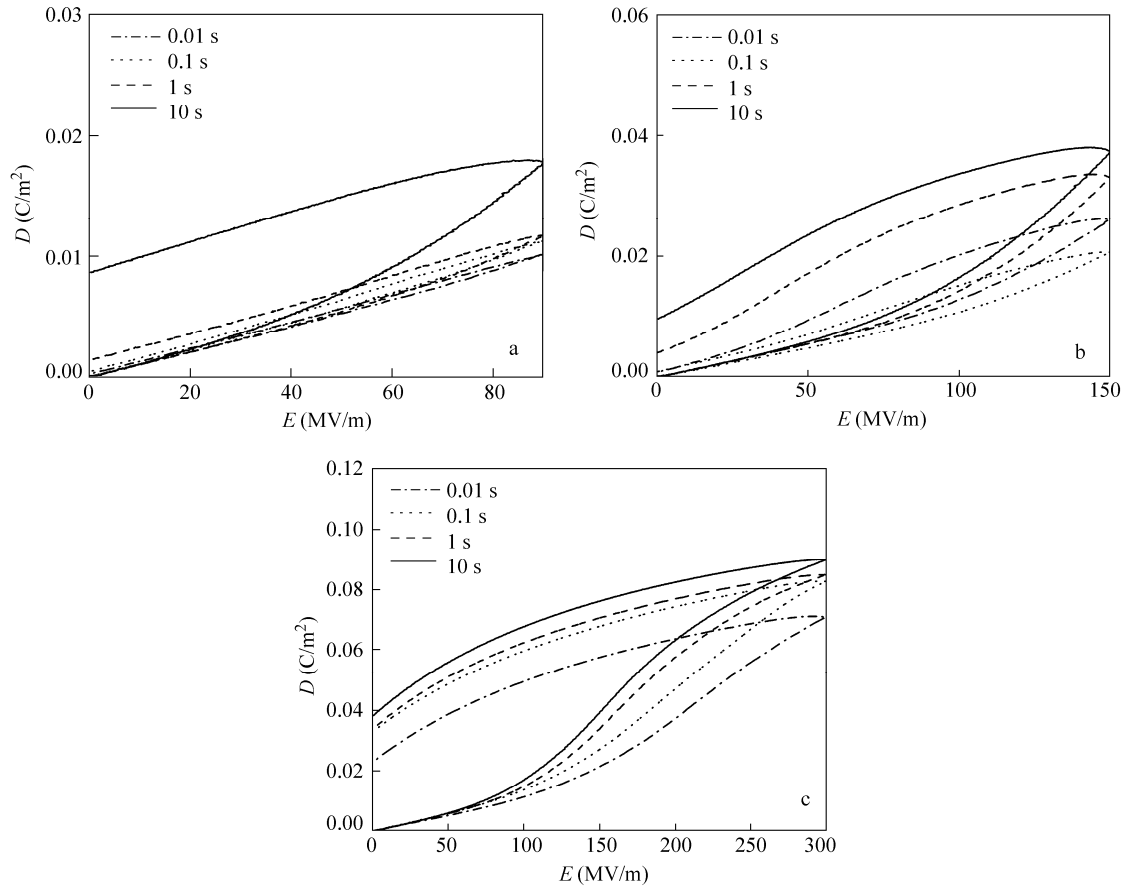


Fig. 7 Unipolar D - E loops for film HPStr90 at various cycle times with different forward poling fields: (a) 90, (b) 150 and (c) 300 MV/m. For each D - E loop measurement, a fresh sample is used.

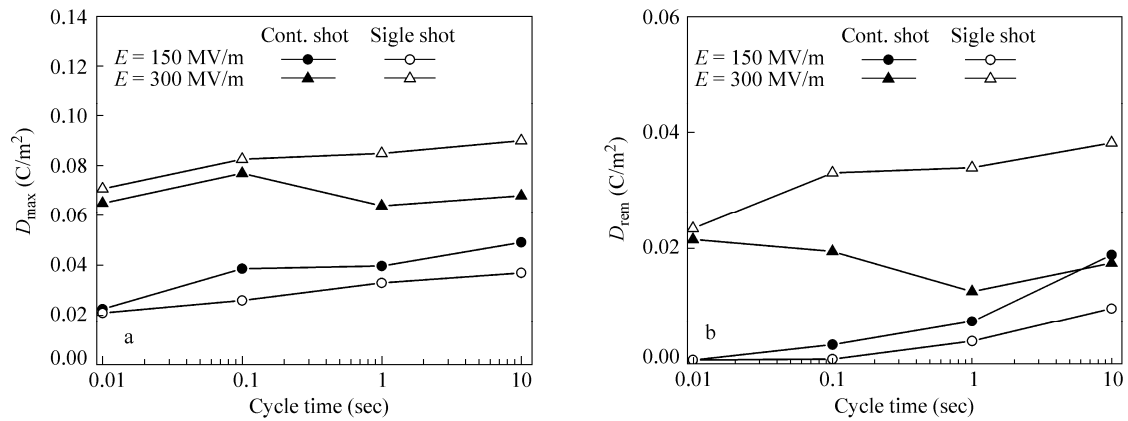


Fig. 8 (a) $D_{\max}$ and (b) D_{rem} as a function of the cycle time for films HPStr90 with continuous and single D - E loop measurements, respectively, at different electric fields. For each single D - E loop measurement, a fresh sample is used.

These differences with and without prior poling history are quantified by comparing $D_{\max}$ and D_{rem} , as shown in Figs. 8(a) and 8(b), respectively. At a low electric field of 150 MV/m, both $D_{\max}$ and D_{rem} were lower for film HPStr90 without prior poling history than for film HPStr90 with prior poling history. At a high electric field of 300 MV/m, both $D_{\max}$ and D_{rem} were higher for film HPStr90 without prior poling history than for film

HPS90 with prior poling history. These results might be explained as the following. For continuous poling experiments, each D - E loop started with an existing D_{rem} in the sample. The D - E loop instrument would auto-zero this existing D_{rem} in order to measure the next D - E loop. Note that this D_{rem} was an undischarged portion of the total polarization in the sample. It was reasonable to assume that the total polarization should be fixed because it depended on the total number of polarizable dipoles in the sample. With auto-zeroing the D_{rem} in continuous poling experiments, the rest amount of polarizable dipoles would actually decrease when compared to the fresh poling. This might be the reason that for fresh poling without prior poling history, the D_{max} could reach a higher value than for continuous poling with prior poling history at high electric fields (e.g., 300 MV/m).

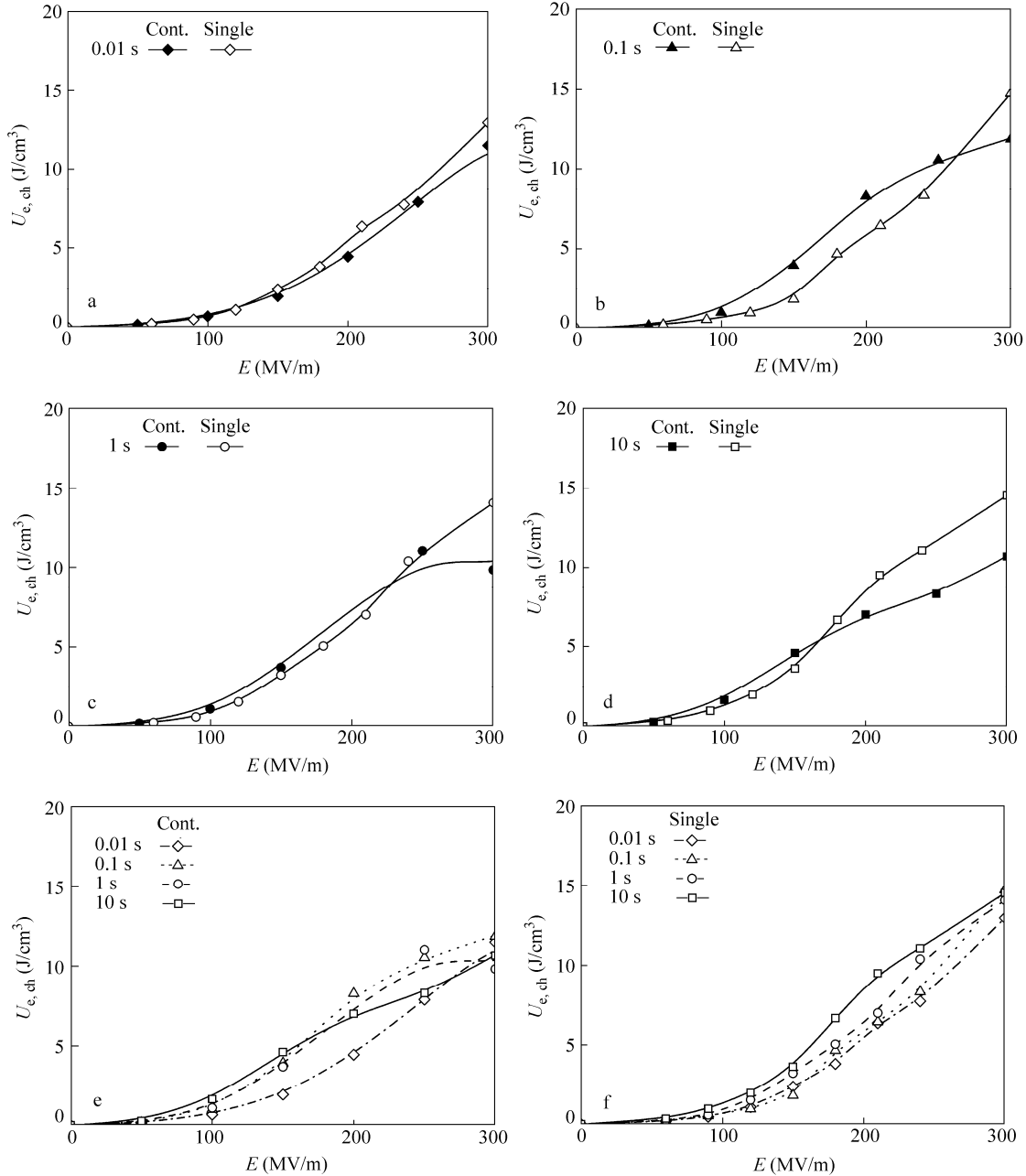


Fig. 9 The charged energy density ($U_{e, \text{ch}}$) as a function of the electric field for films HPStr90 with continuous and single D - E loop measurements at different cycle times: (a) 0.01 s, (b) 0.1 s, (c) 1 s and (d) 10 s, and the $U_{e, \text{ch}}$ as a function of the electric field for HPStr90 with continuous (e) and single (f) D - E loop measurements at various cycle times

However, the situation was different at low electric fields (e.g., 150 MV/m), where the D_{rem} was very low and there was still a large amount of polarizable dipoles to be polarized. Generally, dipole switching could be considered as a first order transition with nucleation and growth processes. This small D_{rem} might actually provide nuclei (*i.e.*, remaining aligned ferroelectric domains) for the next poling cycle to make it easier. Therefore, for continuous poling with prior poling history, the D_{max} could reach a higher value than for fresh poling without prior poling history.

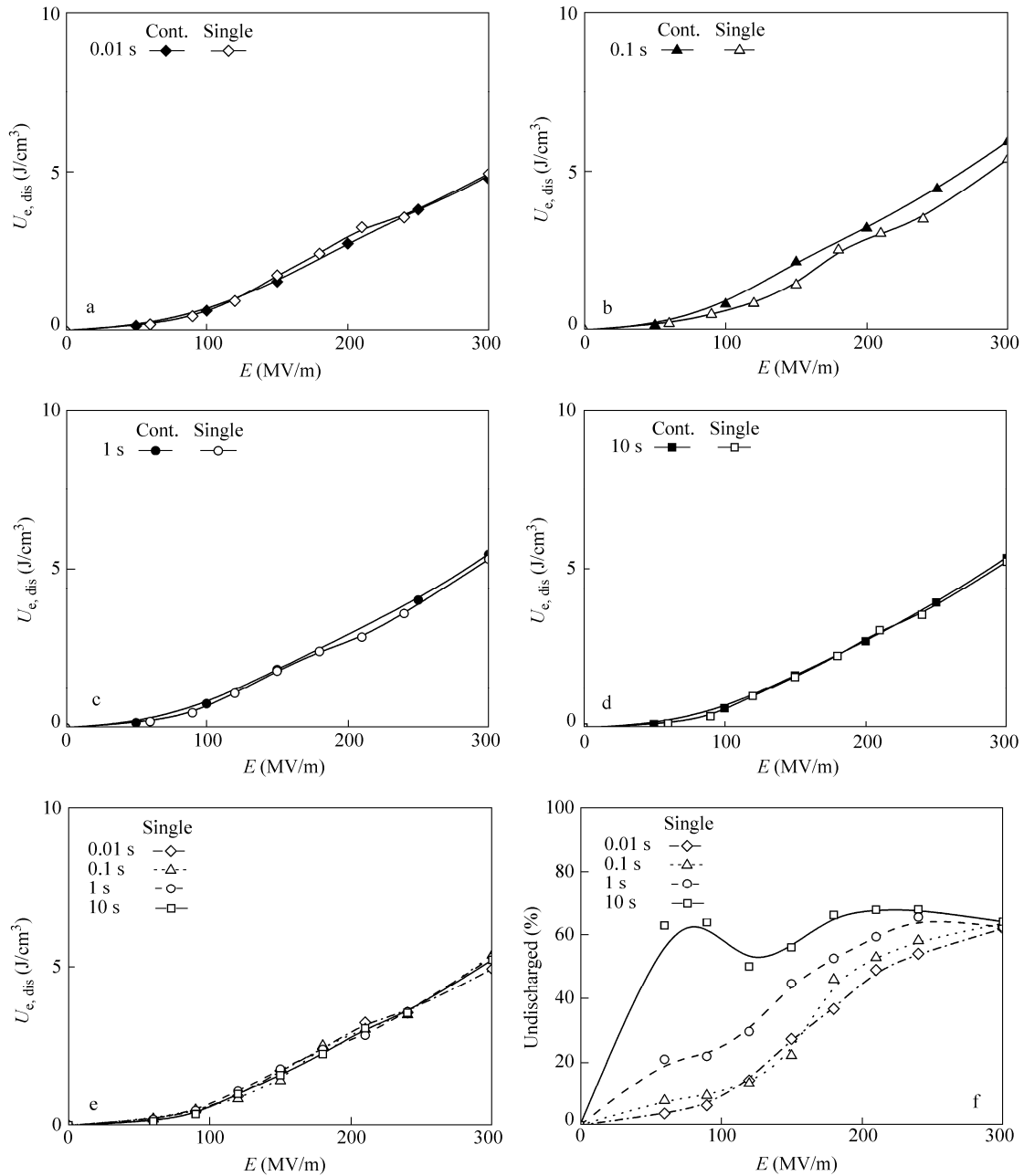


Fig. 10 The discharged energy density ($U_{e, \text{dis}}$) as a function of the electric field for films HPStr90 with continuous and single D - E loop measurements at different cycle times: (a) 0.01 s, (b) 0.1 s, (c) 1 s and (d) 10 s, and the $U_{e, \text{dis}}$ (e) and undischarged (%) (f) as a function of the electric field for HPStr90 with single D - E loop measurements at various cycle times

Comparison of the stored energy densities for continuous poling and fresh poling behaviors at various cycle times is shown in Figs. 9(a)–9(d). There were obvious differences between the two poling methods. Figure 9(f) shows stored energy densities for the fresh poling at different cycle times. Again, the longer the cycle time, the higher the stored energy density.

Figures 10(a)–10(d) show the comparison of discharged energy densities between the continuous poling and fresh poling at various cycle times. Other than the 0.1 s cycle time (the reason for the slightly different discharged energy densities at 0.1 s cycle time is currently not clear), the discharged energy densities were exactly the same for the continuous and fresh poling processes. Figure 10(e) shows the discharged energy densities for the fresh poling at various cycle times. Again, the discharged energy densities were the same despite of different cycle times. Figure 10(f) shows the undischarged (%) as a function of the electric field at various cycle times. Again, with increasing the cycle time, the maximum gradually shifted to lower electric fields, and this obviously originated from the differences in the charged energy densities not the discharged energy densities at different cycle times.

Another experiment was performed to study the effect of consecutive poling on the charging and discharging behaviors for film HPStr90 at different poling fields (150 and 300 MV/m), while keeping other conditions exactly the same (Figs. 11a and 11b). At each poling field, a fresh sample was used, but it was polarized consecutively for four times while keeping the same cycle time of 0.1 s. At a low poling field of 150 MV/m (Fig. 11a), four *D-E* loops superposed. At a high poling field of 300 MV/m (Fig. 11b), the first *D-E* loop was very different from the rest. With increasing the cycle number, it seemed that a steady state was reached for the *D-E* loops. From these *D-E* loops, the charged and discharged energy densities were obtained and shown in Figs. 12(a) and 12(b), respectively. Because the *D-E* loops overlapped at 150 MV/m, the charged and discharged energy densities remain the same for different cycle numbers. However, for the 300 MV/m poling field, the charged energy density decreased after the first cycle and leveled off for the rest of cycles. The discharged energy density again remained nearly the same for different cycle numbers. Figure 12(c) shows the undischarged (%) as a function of the cycle number. Obviously, there was no change at 150 MV/m. At 300 MV/m, the undischarged (%) decreased after the first cycle and leveled off for the rest cycles. Again, the change in the undischarged (%) primarily originated from the variation in the charge energy density rather than the discharged energy density.

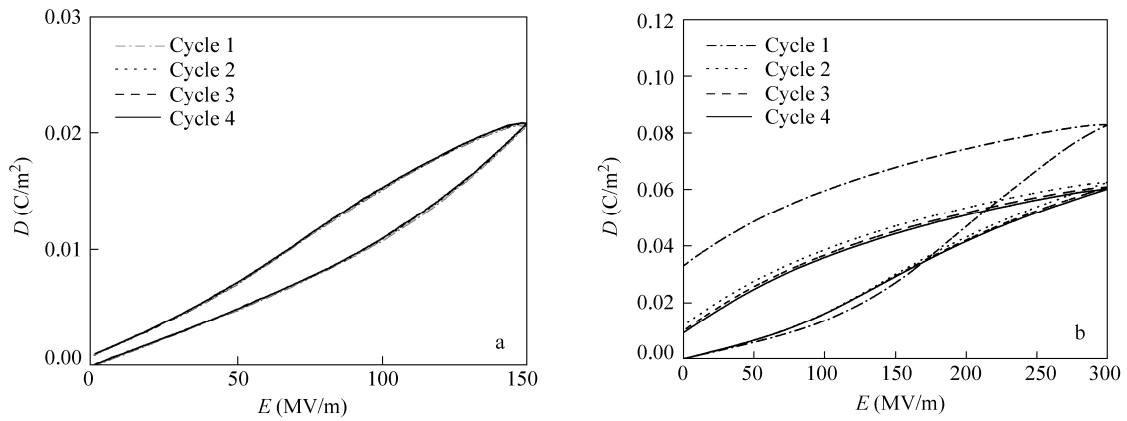


Fig. 11 Unipolar *D-E* loops for film HPStr90 at a poling field of (a) 150 and (b) 300 MV/m. For each poling field, a fresh sample is used and it is polarized consecutively for four times; The cycle time is kept at 0.1 s for all *D-E* loop measurements.

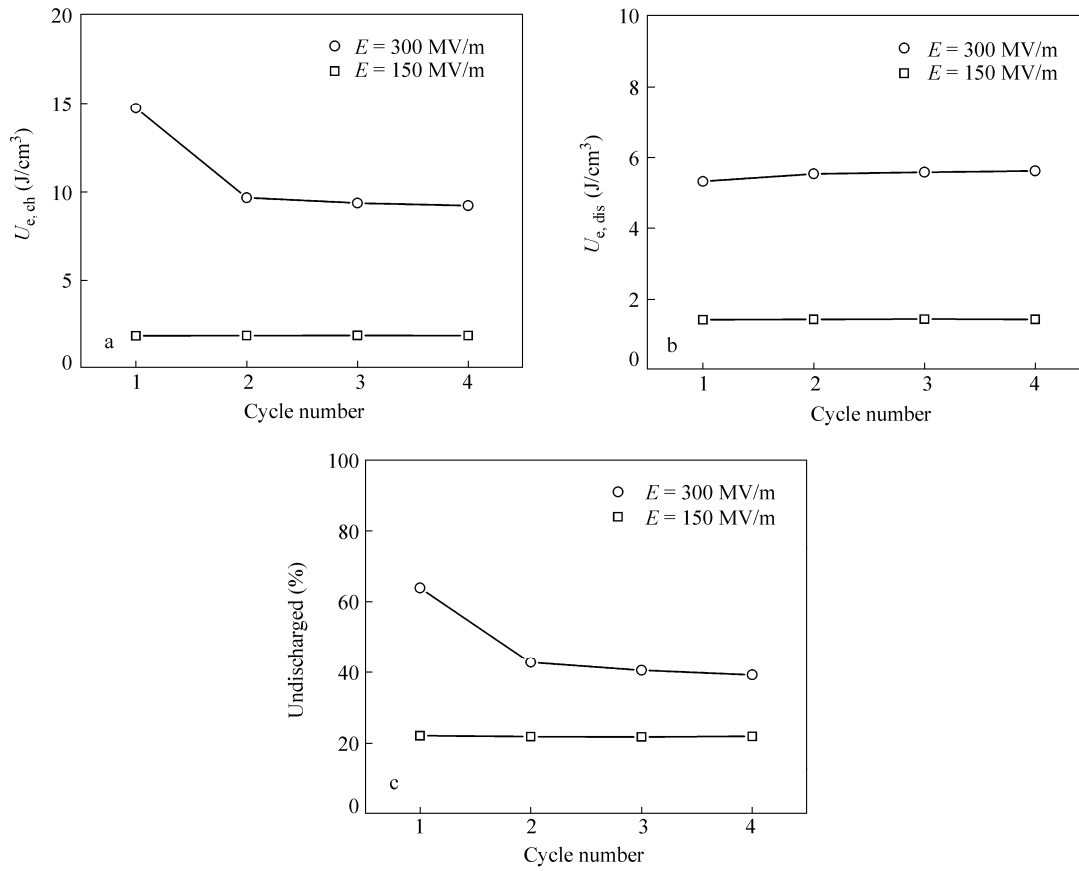


Fig. 12 (a) Charged and (b) discharged energy densities as a function of the cycle number for film HPStr90 at different poling fields, and (c) the undischarged (%) as a function of the cycle number. For each poling field, a fresh sample is used and it is polarized consecutively for four times; The cycle time is kept at 0.1 s for all D - E loop measurements.

From the above experimental results, we can see that the stored energy density for ferroelectric P(VDF-HFP) depends on both cycle time and poling history, while the discharged energy density does not at least in a time frame of 0.01–10 s. Therefore, it is only meaningful to compare the discharged energy densities but not the stored energy densities for ferroelectric polymers because they depend on different ways to measure them. We consider that there must be two types of polarization in P(VDF-HFP) films. One was the reversible fast polarization, which must have a relaxation time much shorter than 10 ms. The other was the irreversible slow polarization, which eventually led to the remnant polarization and has very long relaxation time. From the above results, the irreversible polarization must be orientational in nature and heavily dependent upon the poling time. For a normal ferroelectric PVDF, the reversible polarization was primarily attributed to the deformational (*i.e.*, both electronic and atomic) polarization for both crystalline and amorphous PVDF, and could be discharged very quickly^[31]. The amount of energy density from the reversible polarization is only 10%–20% of the total stored energy density. For our P(VDF-HFP) films, the discharged energy density from the reversible polarization is about 40% at 300 MV/m, much higher than the 10%–20% for normal ferroelectric PVDF. Therefore, the extra 20%–30% energy density must originate from orientational polarization with fast switchable dipoles, and the relaxation time of these fast switching dipoles must be less than 10 ms. This is consistent with recent reports that for PVDF copolymers the discharged energy density levels off after 1–2 ms discharge time^[27, 29]. Therefore, the reversible polarization is actually discharge time dependent, but has a relaxation time less than 1–2 ms. Note that discharged energy densities can be measured by two methods; direct

discharge circuit^[22, 29] and *D-E* loop measurements^[27, 28]. For direct discharge circuit measurements, it usually measures energy density from 1 μ s to 5 ms, while the *D-E* loop measurements can only measure at a cycle time above 10 ms due to the limitation of the instrument.

On the basis of our previous reports, we speculate that the fast reversible polarization in P(VDF-CTFE) and P(VDF-HFP) originates from nanoconfined decoupled dipoles or ferroelectric domains because the crystallite sizes are much smaller than those in pure PVDF. The irreversible polarization should originate from highly coupled dipoles or ferroelectric domains, which are easier to be polarized but difficult to be depolarized^[16]. By decoupling the dipoles/ferroelectric domains, the switching back of dipoles/ferroelectric domains to a random state during discharging will become faster and thus more energy can be released^[16]. Currently, the challenge for the high electric energy storage using ferroelectric polymers is how to effectively convert the irreversible polarization into the reversible polarization. More theoretical and experimental works are desired for future study.

CONCLUSIONS

In this work, we studied cycle time (0.01–10 s) and poling history (continuous versus fresh poling) dependent charging and discharging behaviors in P(VDF-HFP) films. Intriguingly, the charging process depended heavily on the cycle time and prior poling history, while the discharged energy density did not in this particular time range. This experimental result could be explained by reversible and irreversible polarizations in the films. The reversible polarization could be charged and discharged very quickly (< 5 ms for each process), while the irreversible polarization heavily depended on the poling time and prior poling history. On the basis of this study, it is only meaningful to compare the discharged energy density for PVDF and its copolymer films when different cycle times and poling histories are used.

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