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# Electric energy storage properties of poly(vinylidene fluoride)

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High discharged energy density observed in poly(vinylidene fluoride) (PVDF) based copolymers has attracted considerable research interests in the past years. Crystalline properties exhibit great influence on their dielectric and energy storage properties. To understand how crystalline properties influence the energy storage properties of PVDF, PVDF films with three different crystal forms are investigated in this paper. It is shown that  $\gamma$ -PVDF is allowed to work under higher electric fields than  $\alpha$ - and  $\beta$ -PVDF in the absence of phase transition in  $\alpha$ -PVDF and early polarization saturation in  $\beta$ -PVDF. Consequently,  $\gamma$ -PVDF exhibits the highest energy density of 14 J/cm<sup>3</sup> under 500 MV/m electric field. © 2010 American Institute of Physics. [doi:10.1063/1.3428656]

High energy density pulse discharge capacitor is an important electric energy storage unit and widely utilized in electromagnetic generation, Marx generators, pulsed laser, and particle accelerators. Currently, the dielectric film applied in high pulse discharge capacitors is mainly made of biaxially oriented polypropylene with an energy density of 2.5 J/cm<sup>3</sup> below 600 MV/m electric field. Recently, poly(vinylidene fluoride) (PVDF) based ferroelectric copolymers for high energy storage purpose have attracted considerable interests.<sup>1–4</sup> We have systematically reported the crystallization, dielectric, and energy storage properties of VDF, trifluoroethylene (TrFE), and chlorotrifluoroethylene (CTFE) copolymers.<sup>5</sup> The introduction of CTFE into ferroelectric P(VDF-co-TrFE) converts its polymer chain from *all-trans* (TTTT) conformation ( $\beta$ -phase) into *trans-trans-trans-gauche* (TTTG) chain conformation ( $\gamma$ -phase) in P(VDF-co-TrFE-co-CTFE). Meanwhile, the crystallinity of the copolymer is reduced, which provides essential lattice space for the poling and reversing of dipoles under high electric fields. As a result, the copolymer in  $\gamma$  phase with optimized crystallinity and crystal domain size exhibits an energy density as high as 17 J/cm<sup>3</sup>. More recently, even higher energy density (26 J/cm<sup>3</sup>) is obtained in uniaxially stretched P(VDF-co-CTFE) 91/9 mol % film.<sup>6</sup> The existence of Cl atom may stabilize the nonpolar  $\alpha$ -phase of the copolymer, which allows the copolymer to work under higher electric fields without early polarization saturation. It seems that the nonpolar  $\alpha$  phase instead of polar phase favors improving the applied electric field onto the copolymers, thus their energy storage capacities.

It has been well known that neat PVDF has four different crystal forms including  $\alpha$  [in *trans-gauche* conformation (TGTG)],  $\beta$  [in *all trans* planar zigzag conformation (TTTT)],  $\gamma$  [in a conformation of three *trans* linked to a *gauche* (TTTG)], and  $\delta$  phase (a polar version of the  $\alpha$  phase) depending on the processing conditions.<sup>7</sup> Although the dielectric, piezoelectric and ferroelectric properties of PVDF in

different phases especially  $\beta$ -PVDF have been well studied.<sup>8</sup> However, how the different crystal phases influence the energy storage properties of neat PVDF is still not clear. In this work, the energy storage properties of the PVDF films with different crystal phases are well investigated.

Untreated  $\alpha$ -PVDF film in a thickness of 20–30  $\mu$ m is prepared via casting the PVDF solution in dimethylformamide onto a glass substrate followed by drying at 100 °C for 24 h. The quenched or annealed  $\alpha$ -PVDF film is prepared via heating the untreated film at 200 °C for 30 min followed by immediately quenching in ice-water bath or cooling gradually in an oven in 24 h. The uniaxially stretched  $\beta$ -PVDF film (30  $\mu$ m thick) coated with aluminum on both sides as electrode is supplied by Jinzhou Kexin Dianzi Cailiao Co., Ltd.  $\gamma$ -PVDF is prepared via solution casting at 40 °C (untreated film) followed by heating at 200 °C for 5 min and immediately quenching in ice-water bath (quenched) or cooling gradually in an oven in 24 h (annealed). X-ray diffraction (XRD) analysis is obtained on a RIGAKU D/MAX-2400 (Rigaku Industrial Corporation, Japan). Difference scanner calorimeter (DSC) analysis is conducted on a NETZSCH DSC 200 PC (NETZSCH Corporation, Germany) in nitrogen atmosphere. For electric characterizations, gold electrodes (about 80 nm) are sputtered on both surfaces of the  $\alpha$ - and  $\gamma$ -PVDF films. The electric displacement-electric field (D-E) hysteresis loops are measured with a modified Sawyer-Tower circuit and a linear variable differential transducer, driven by a lock-in amplifier (Stanford Research Systems, model SR830).

Figure 1 presents the XRD of PVDF in three different crystal phases. In  $\alpha$ -PVDF film, the peaks at  $2\theta=17.9^\circ$ ,  $18.4^\circ$ ,  $20.2^\circ$ ,  $27.9^\circ$ ,  $36.1^\circ$ , and  $39.0^\circ$  are assigned to (110), (020), (021), (111), (200), and (002) reflections of  $\alpha$  phase crystal plane, respectively. The peak at  $2\theta=26.8^\circ$ , attributed to the (022) reflection of  $\gamma$  crystal plane, indicates the existence of minority of  $\gamma$ -PVDF. In  $\gamma$ -PVDF film, the peaks at about  $18.5^\circ$ ,  $20.1^\circ$ , and  $38.7^\circ$  are (020), (110), and (211) reflections of the  $\gamma$  phase crystal plane, respectively. The peak at  $39^\circ$  is evidenced the existence of  $\alpha$ -PVDF in small quantity. In the uniaxially stretched film, the peaks at  $20.7^\circ$ ,

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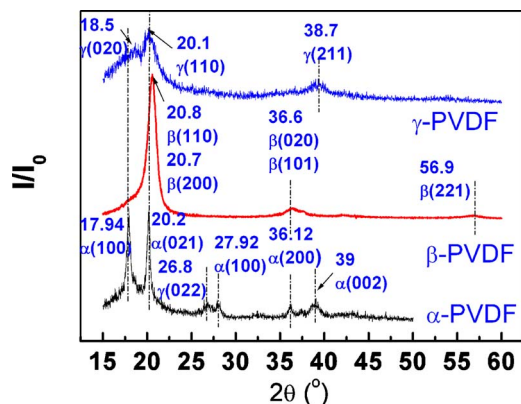


FIG. 1. (Color online) XRD and assignment of PVDF with  $\alpha$ -,  $\beta$ -, and  $\gamma$ -form crystal phases.

36.6°, and 56.9° are assigned to (110, 200) (020, 101), and (221) reflections of  $\beta$ -PVDF crystal plane, respectively.<sup>9</sup> The phase structure of the three PVDF films could also be confirmed by Fourier transform infrared (FTIR) spectroscopy as shown in Fig. S1 in Ref. 10.

Figure 2 presents the D-E loops of PVDF with three different crystal phases measured under ac (a) and dc (b) electric field at 10 Hz. Under ac field, a typical ferroelectric D-E loop characterized with a high remnant polarization is observed in  $\beta$ -PVDF due to its all-*trans* polymer chain. D-E loops of  $\alpha$ - and  $\gamma$ -PVDF are quite close, where the remnant polarization of  $\gamma$ -PVDF is slightly higher than that of  $\alpha$ -PVDF. That may be attributed to the TTTG conformation of  $\gamma$ -PVDF possessing higher polarity than that of TGTG chain conformation in  $\alpha$ -PVDF. Meanwhile, the maximum displacement of  $\beta$ -PVDF is much higher than that of  $\alpha$ - and  $\gamma$ -PVDF under the same electric field. That means  $\beta$ -PVDF would reach the displacement saturation under a much lower electric field than  $\alpha$ - and  $\gamma$ -PVDF since their overall dipole moments are the same. The major difference of D-E loops measured under ac and dc electric field is the reflection of irreversible polarization in the materials. As shown in Fig. 2(b), the polarization of  $\beta$ -PVDF under 150 MV/m dc electric field is 0.024 C/m<sup>2</sup> while it is 0.068 C/m<sup>2</sup> under ac field, which indicates that about 60% of the polarization (0.044 C/m<sup>2</sup> in amount) is not reversible. This part of polarization makes no contribution to the energy storage since the electric energy charged is not dischargeable. However, the irreversible polarization of  $\alpha$ - and  $\gamma$ -PVDF under 200 MV/m field is only about 0.01 C/m<sup>2</sup> (20% in total). That indicates that  $\alpha$ - and  $\gamma$ -PVDF with lower polarity exhibit higher energy storage efficiency than that of  $\beta$ -PVDF in electric energy charging-discharging circles.

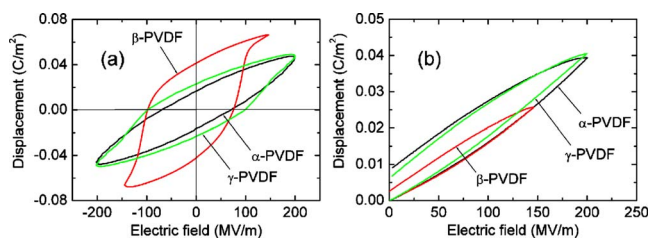


FIG. 2. (Color online) D-E hysteresis loops of PVDF in different crystal phases measured under ac (a) and dc (b) electric field. ( $\alpha$ - and  $\gamma$ -PVDF films are quenched samples, and  $\beta$ -PVDF film is uniaxially stretched.)

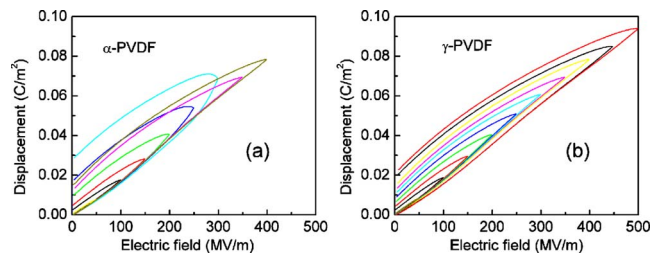


FIG. 3. (Color online) Unipolar D-E hysteresis loops of quenched  $\alpha$ -PVDF (a) and  $\gamma$ -PVDF (b) film as a function of electric field.

The D-E loops of the  $\alpha$ - and  $\gamma$ -PVDF films are measured as a function of dc electric field as presented in Fig. 3. According to the discharged energy density formula  $U_e = \int E dD$  of nonlinear dielectric materials, the electric field allowed to be applied on them is as important as the displacement to achieve the high energy density. D-E loops of  $\alpha$ -PVDF are growing in parallel with the electric field before a sudden shrink is observed under the electric field of 300–350 MV/m. XRD results indicate that  $\alpha$ -PVDF has been fully converted into  $\gamma$  phase when an electric field of over 300 MV/m is applied on  $\alpha$ -PVDF as shown in Fig. S2. In  $\gamma$ -PVDF, the D-E curves measured under increasing dc electric field are rather slim. Interestingly,  $\gamma$ -PVDF is allowed to be applied under an electric field as high as 500 MV/m and the corresponding displacement obtained is over 0.09 C/m<sup>2</sup>, which is rather close to the theoretical saturation displacement (0.13 C/m<sup>2</sup>) counting the irreversible polarization (about 20%). The unipolar D-E loops of  $\beta$ -PVDF as a function of electric field are presented in Fig. S3. All the D-E curves are as slim as that of  $\gamma$ -PVDF obtained under the same electric field. However, the maximum electric field allowed to be applied on  $\beta$ -PVDF is less than 200 MV/m for its early displacement saturation. As a result, the highest polarization in unipolar D-E loop is obtained as only 0.027 C/m<sup>2</sup> under 150 MV/m dc field for its high remnant polarization.

Figure 4 presents the discharged energy density and loss of PVDF with different crystal forms, which are calculated from the unipolar D-E loops of the films. Under the electric field below 200 MV/m, both the discharged energy density and energy loss of three PVDF films are rather close. The energy density and loss of  $\beta$ -PVDF under electric fields beyond 200 MV/m are not available for its displacement saturation. The energy density of  $\alpha$ -PVDF is mostly slightly higher than that of  $\gamma$ -PVDF under the same electric field. The phase transition from  $\alpha$  to  $\gamma$  phase occurs in  $\alpha$ -PVDF may account for its lower discharged energy density than  $\gamma$ -PVDF under 300 MV/m field. In addition, higher energy

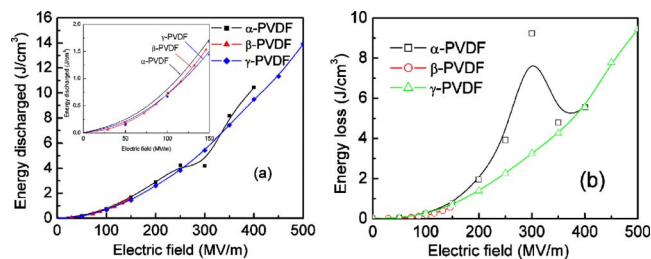


FIG. 4. (Color online) Energy density (a) and loss (b) of PVDF with different crystal phases as a function of electric field. ( $\alpha$ - and  $\gamma$ -PVDF films are quenched samples, and  $\beta$ -PVDF film is uniaxially stretched.)

loss values of  $\alpha$ -PVDF than  $\gamma$ -PVDF are mainly observed under the electric field of 150–350 MV/m. Apparently, some of the energy charged, instead of being discharged once the electric field is removed, is involved in the polymer chain conformation conversion from TGTG in  $\alpha$ -phase to TTTG in  $\gamma$ -phase. Once the phase transition completes, both the energy density and loss of  $\alpha$ - and  $\gamma$ -PVDF films coincide very well. Among the PVDF films with different crystal phases, only  $\gamma$ -PVDF could be applied under the high electric field (500 MV/m) in the absence of phase transition in  $\alpha$ -PVDF and early polarization saturation in  $\beta$ -PVDF. As a result, a discharged energy density as high as 14 J/cm<sup>3</sup> is achieved.

In summary, the energy storage properties of PVDF with three different crystal domain forms are studied under increasing electric fields. It is obtained that PVDF in three crystal forms possesses the similar energy density and loss under low electric fields. PVDF in  $\beta$ -phase may not be applied under electric fields beyond 200 MV/m for its early displacement saturation, and its maximum discharged energy density is the lowest (1.5 J/cm<sup>3</sup> at 150 MV/m).  $\alpha$ -PVDF could only survive in the electric field below 300 MV/m for the phase transition of  $\alpha$  to  $\gamma$  phase under the electric field of 200–350 MV/m.  $\alpha$ -PVDF has the similar energy density but higher energy loss than  $\gamma$ -PVDF in the electric field below 350 MV/m. Only the quenched  $\gamma$ -PVDF is able to survive under electric fields beyond 350 MV/m and the highest dis-

charged energy density is obtained as 14 J/cm<sup>3</sup>, which is more desirable for high pulse discharge capacitor application than the other two PVDF films.

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<sup>10</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3428656> for the FTIR, XRD, DSC, dielectric constant and loss of  $\alpha$ - and  $\gamma$ -PVDF treated in different process, XRD of poled  $\alpha$ -PVDF in an electric field beyond 300 MV/m and the unipolar D-E loops of  $\beta$ -PVDF as a function of electric field.