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Study of VDF/TrFE/CTFE Terpolymers for High Pulsed Capacitor with High Energy Density and Low Energy Loss

Zhicheng Zhang and T. C. Mike Chung*

Department of Materials Science and Engineering,
The Pennsylvania State University,
University Park, Pennsylvania 16802

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Opposite to battery technology, which has high energy density and low power density, capacitors[1−3] usually exhibit high powder density but very low energy density. The capacitor energy density is directly governed by the dielectric material that separates the opposite static charges. The energy density can be estimated by the equation $(\mathrm{J/cm^3}) = {}^1/_2\epsilon E^2 = {}^1/_2\epsilon(V/d)^2$, wherein ϵ is the dielectric constant of the dielectric and E is the applied electric field. The ideal dielectric material should be able to form uniform (defect-free, impurity-free, and mechanic-strong) thin film with a small thickness (d) and suitable morphology that allows the application of high voltage (V) across the film.

The metallized polymer film capacitors[4,5] show many desirable properties, such as light weight, low cost, excellent processability to form tough thin film, ability to be packed into a desirable configuration, and self-healing,[6] so that they can be operated near the breakdown voltage. Despite the low dielectric constant ($\epsilon = 2.2$), biaxial oriented polypropylene[7,8] thin film produces decent releasing energy density (1−1.2 J/cm^3) after applying to 640 MV/m. The usage of high dielectric poly(vinylidene fluoride)[9] showed mixed results. Although the capacitor with energy density of 2.4 J/cm^3 was observed,[10] the combination of a nonlinear response to the voltage, high remnant polarization, and high energy loss makes the capacitor performance difficult to predict.[7] A report showed poor performance in vinylidene fluoride/trifluoroethylene copolymers[13] with low energy density ($<$1 J/cm^3) and very high energy loss. Better results were shown in the corresponding irradiated composite material,[11] containing high dielectric ceramic ferroelectric relaxor, which showed that the energy density increases to about 1.8 J/cm^3 at a relatively low electric field (80 MV/m). A recent report showed high energy density in a vinylidene fluoride/chlorotrifluoroethylene (91/9 mol %) copolymer[12] with nonspecific energy loss and remnant polarization. It is worthwhile to further investigate this family of fluoropolymers, with the objective of identifying the molecular structure showing a good combination of high breakdown electric field, high releasing energy density, low energy loss, and no remnant polarization after the discharge cycle.

In this paper, we examine a family of modified PVDF polymers (Scheme 1) that contains vinylidene difluoride (VDF), trifluoroethylene (TrFE), and chlorotrifluoroethylene (CTFE) units.[13] The consecutive VDF units provide strong polarization, the randomly distributed TrFE units (cocrystallizable with VDF units) direct the VDF sequence to all-trans (polar) conformation, and the small amounts of bulky Cl atoms in CTFE units serve as the kinks to reduce the crystalline size without significantly reducing the overall crystallinity. Some terpolymers exhibit high dielectric constant and relaxed ferroelectric behaviors.[14,15] It is logical to think that this type of terpolymer with a particular composition might show high energy density (due to high dielectric constant and breakdown voltage) and low energy loss (due to relax ferroelectric behavior).

Table 1 summarizes two comparative sets of VDF/TrFE/CTFE terpolymers with a systematic variation of TrFE and CTFE contents. To obtain high quality terpolymers (high purity and narrow molecular weight and composition distributions), we employed borane/oxygen-mediated control radical polymerization[16,17] in a homogeneous acetonitrile solution at ambient temperature. The synthesis and structure characterization are discussed in the Supporting Information. Figures 1S and 2S (see plots in the Supporting Information) show DSC curves of two sets of VDF/TrFE/CTFE terpolymers. The relatively sharp melting peak in all co- and terpolymers implies a relatively uniform molecular structure and morphology. In Figure 1S, the increase of CTFE units (by substituting TrFE units) systematically reduces both melting (T_m) and Curie (T_c) temperatures, but maintaining high heat of fusion (ΔH) that starts its diametrical descent after the CTFE content reaches $>$8 mol %. In Figure 2S, the terpolymers with ∼7.5 mol % CTFE units and various VDF/TrFE mole ratios maintain an overall high crystallinity. The VDF/TrFE (63.3/36.7 mol %) copolymer shows an expected Curie temperature at 65 °C. With ∼7.5 mol % of CTFE content, the terpolymer Curie temperature shifts to near ambient temperature, and the intensity becomes very weak, indicating a relaxed ferroelectric behavior.

Figure 1 compares the dielectric constant between VDF/CTFE (92/8 mol %) copolymer and VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer. The dielectric constant profile provides a sharp Curie transition temperature. The polymers containing less than 15 mol % TrFE units show no Curie temperature (Figure 3S), which may be too high to be observed. It is necessary to have more than 20 mol % of TrFE units to observe the Curie temperature, which shifts rapidly toward the ambient temperature as the TrFE content increases toward 35%. In other words, the dielectric constant profile (polarization of CF$_2$ dipoles) can be effectively controlled by terpolymer composition and thermal energy. It is engrossing to understand the similar polarization−depolarization effect under the applied electric field.

Figure 2 compares $D-E$ (charge displacement vs unipolar electric field) hysteresis curves[18] of the same set of VDF/CTFE and VDF/TrFE/CTFE polymers, with similar CTFE content (7.7−8.0 mol %). The charging−discharging cycles were first applied to 100 MV/m and then increasing 50 MV/m intervals until reaching the breakdown electric field. It is important to note that the thin film quality has a great effect on the breakdown electric field. To ensure uniform and defect-free thin films for side-by-side comparison at equilibrium state, all polymers were solution cased into approximately 30−40 μm thick films. The films were then conditioned in a vacuum oven at melting temperature for a few hours before slowly cooling to room temperature in order to obtain transparent uniform films 10−15 μm thick. At least five samples were tested in each composition in order to minimize any possible errors ($<$10%). Without TrFE unit, the breakdown electric field for VDF/CTFE (92/8 mol %) copolymer (A-1) is typically 350 MV/m, and the copolymer shows a large hysteresis in polarization−depolarization curves with high-energy loss and large remnant polariza-

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* To whom all correspondence should be addressed. E-mail: chung@ems.psu.edu.

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Scheme 1

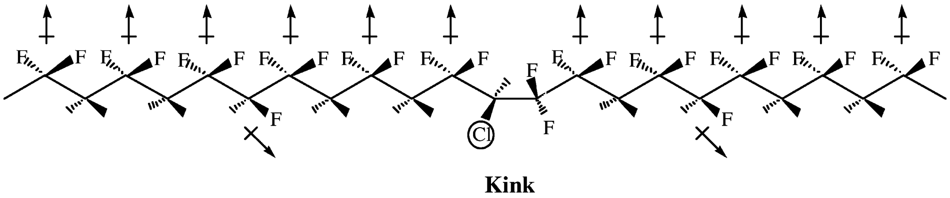

Table 1. Summary of Two Comparative Sets of VDF/TrFE/CTFE Terpolymers Prepared by Triethylborane/Oxygen Radical Initiator

run	B/O$_2$ (mol/mol)	VDF/TrFE/CTFE (mL)	time (h)	cov (%)	VDF/TrFE/CTFE (%)	T_m (°C)	T_c (°C)	ΔH (J/g)
A-1	0.3/0.4 (TEB)	20.0/18.0/2.0	3	25	58.4/34.2/7.4	121.5	19.8	20.6
A-2	0.3/0.4 (TEB)	20.0/11.6/1.5	3	38	65.6/26.7/7.7	123.6	23.8	22.0
A-3	0.3/0.4 (TEB)	25.0/4.3/1.0	4	32	80.7/11.6/7.7	120.1	N.A	27.9
A-4	0.3/0.4 (TEB)	25.0/0.0/1.5	5	28	92.0/0.0/8.0	145.0	N.A	25.9
B-1	0.3/0.4 (TEB)	20.0/18.0/0.0	3	26	63.3/36.7/0.0	151.7	64.6	30.1
B-2	0.3/0.4 (TEB)	20.0/20.0/1.5	3	20	58.3/37.4/4.3	134.6	31.2	23.3
B-3	0.3/0.4 (TEB)	20.0/20.0/2.0	3	22	56.2/37.0/6.8	121.3	18.8	21.3
B-4	0.3/0.4 (TEB)	20.0/18.0/2.0	3	25	58.4/34.2/7.4	121.5	19.8	20.6
B-5	0.3/0.4 (TEB)	20.0/20.0/2.5	3	21	57.1/31.4/11.5	106.4	N.A	17.0

tion at the end of each cycle (zero electric field). The initial increase of the TrFE content seems to have a very small effect to the *D*−*E* hysteresis curves. The significant changes were only observed while the TrFE content reached >20 mol % (Figure 4S). The VDF/TrFE/CTFE (65.6/26.7/7.7) terpolymer (A-3), with the Curie temperature at around 35−40 °C, shows the highest breakdown electric field at >500 MV/m and slim polarization−depolarization curves with low energy loss and almost no remnant polarization. The electric displacement reaches to about 0.1 C/m^2 at 500 MV/m. Compared with the theoretical electric displacement of 0.13 C/m^2 for the fully

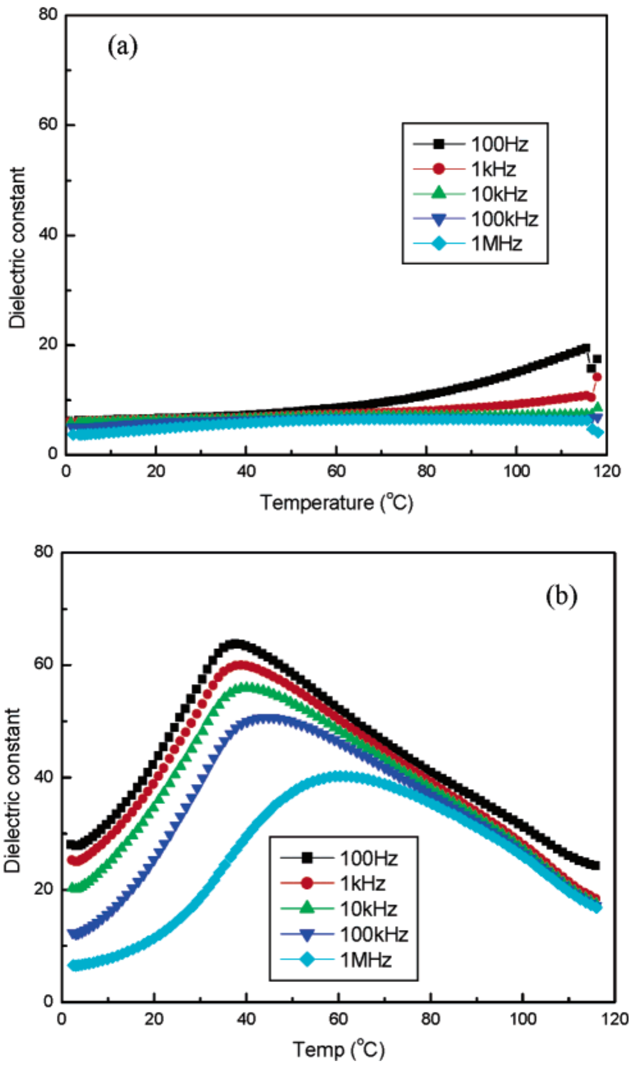

Figure 1. Dielectric constant of (a) VDF/CTFE (92/8 mol %) copolymer (run A-1) and (b) VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (run A-3).

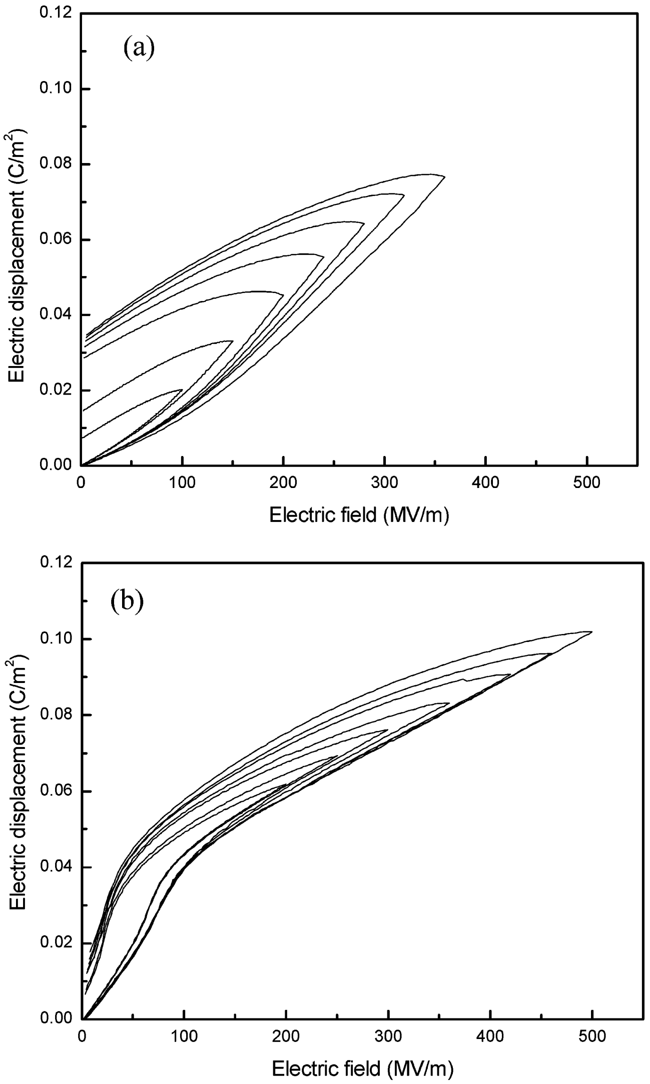

Figure 2. *D*−*E* hysteresis curves of (a) VDF/CTFE (92/8 mol %) copolymer (run A-1) and (b) VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (run A-3).

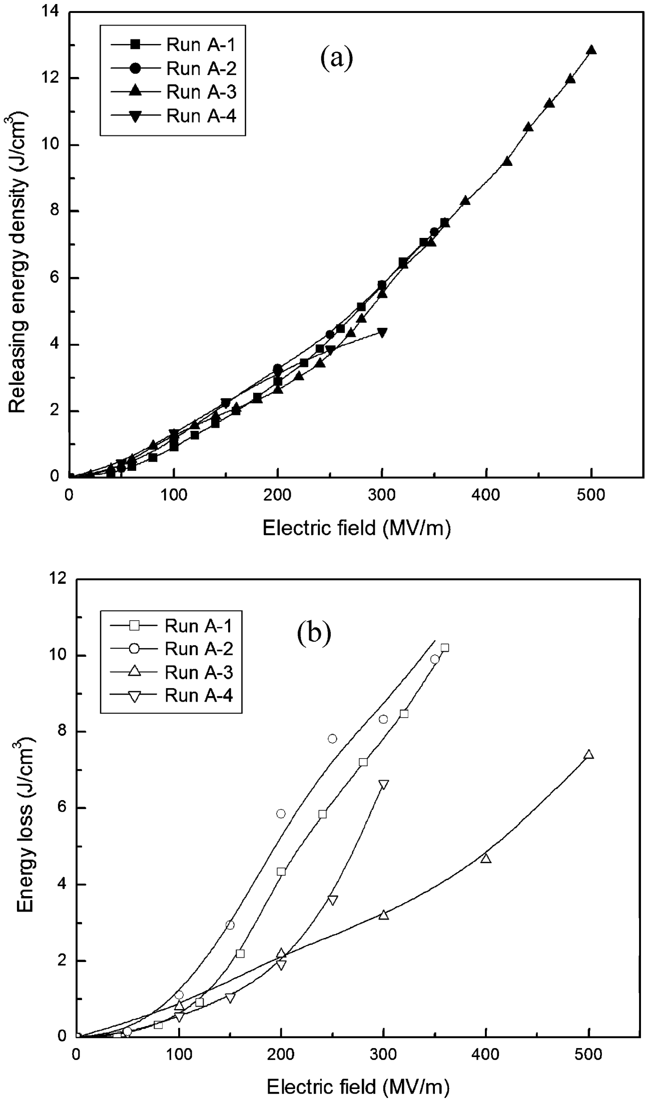

Figure 3. (a) Releasing energy density and (b) energy loss of VDF/CTFE copolymer (run A-1) and three VDF/TrFE/CTFE terpolymers (runs A-2, A-3, and A-4). The solid curves are only used for guiding the eyes in order to see the trend.

polarized (β-phase) PVDF homopolymer,[19] this terpolymer is almost at its limit with almost all VDF and TrFE units polarized along the electric field. With the further increase of the TrFE content (>30%), the polarization−depolarization curves broaden again. The VDF/TrFE/CTFE (58.4/34.2/7.4) terpolymer (Figure 4S) reduces the breakdown electric field back to 350 MV/m and enlarges the polarization−depolarization hysteresis curves with significantly higher energy loss and remnant polarization. In addition, the polarization seems to be saturated at 200 MV/m.

Figure 3 compares releasing energy density (the integrating area under depolarization curve vs electric displacement) and energy loss (the integrating area between polarization and depolarization curves) of the polarization−depolarization cycle (with the maximum electric field) for the same set of co- and terpolymers with CTFE content ~7.5 mol %. In most cases (except A-4, discussed later), the energy density closely follows the same master curve. The releasing energy density increases with the increase of the applied electric field, and the higher breakdown electric field offers the higher energy density. Both VDF and TrFE units in the polymer chain contribute to the electric displacement and energy density. However, the energy loss is dramatically different. For the VDF/CTFE (92/8 mol %) copolymer (A-1) and VDF/TrFE/CTFE (80.7/11.6/7.7) (A-2), with no and low TrFE content and without observing the Curie temperature, the energy loss is very high (even higher than the energy released in all cycles), which is unacceptable in the capacitor design. A dramatic improvement is shown in the VDF/TrFE/CTFE (65.6/26.7/7.7) terpolymer (A-3). It shows not only the highest breakdown electric field (>500 MV/m) and highest energy density (13 J/cm^3), but also lowest energy loss. On the other hand, the energy density curve of the VDF/TrFE/CTFE (58.4/34.2/7.4) terpolymer (A-4) shows a clear deviation from the master curve, with saturation of about 200 MV/m and maximum releasing energy density of only about 4 J/cm^3. The energy loss also shapely increases after 200 MV/m, indicating that all the energy charged is lost after 200 MV/m.

In summary, this paper systematically studies PVDF-based co- and terpolymers to tune its polarization profile for capacitor applications. The desirable terpolymer (VDF/TrFE/CTFE = 65.6/26.7/7.7), exhibiting a high dielectric constant ($\epsilon \sim 60$, 1 kHz) at the Curie temperature (35−40 °C), shows a high breakdown electric field >500 MV/m, high energy density (releasing >13 J/cm^3), relatively small energy loss, and almost no remnant polarization at zero electric field.

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Supporting Information Available: Polymerization procedures and DSC, dielectric constant, and *D*−*E* curves of co- and terpolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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