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14. ABSTRACT

In this program, Penn State, TRS Technologies, and ECI working together to perform a preliminary investigation on various issues related to the ferroelectric relaxor terpolymer for energy storage capacitors. In this program, terpolymers of P(VDF-TrFE-CFE) with different compositions have been synthesized and some of these terpolymers have been fabricated into thin films at ECI; the electric energy density, the AC and DC resistivities of the terpolymers have been characterized; and graceful failure and improvement in the breakdown strength and graceful failure of the terpolymer films were investigated; a high voltage and high speed discharge circuit has been designed and built. The results are summarized in the following.

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Relaxor Terpolymers for Energy Storage Capacitors

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Summary:

In this program, Penn State, TRS Technologies, and ECI working together to perform a preliminary investigation on various issues related to the ferroelectric relaxor terpolymer for energy storage capacitors. In this program, terpolymers of P(VDF-TrFE-CFE) with different compositions have been synthesized and some of these terpolymers have been fabricated into thin films at ECI; the electric energy density, the AC and DC resistivities of the terpolymers have been characterized; and graceful failure and improvement in the breakdown strength and graceful failure of the terpolymer films were investigated; a high voltage and high speed discharge circuit has been designed and built. The results are summarized in the following.

1. Terpolymer synthesis and evaluation

During this time period, 5 different compositions of P(VDF-TrFE-CFE) have been synthesized: ISL15, 16, 17, 18, and 19. The compositions of these terpolymers and batch size are summarized in Table 1. (For the easy comparison with P(VDF/TrFE) copolymer and irradiated copolymer, compositions are also written in (VDF/TrFE)/CFE in (x/(1-x))/y in the 4th column of the Table)

Table 1:

Polymer	Composition	Batch size	Composition in (VDF/TrFE)/CFE units
ISL15:	60/33/7	85 grams	64.5/35.5/7
ISL16:	61.5/30.3/8.2	1 kg	67/33/8.2
ISL17:	64.3/27.6/8.1	1 kg	70/30/8.1
ISL18:	42.9/50.3/6.8	245 grams	46/54/6.8
ISL19:	48.1/45.7/6.2	100 grams	51.3/48.7/6.2

The dielectric properties of these compositions have been characterized. The overall film quality was also evaluated and it was found that the resin reproducibility is still an issue and resin quality is very sensitive to the synthesis parameters which are not well understood at this stage, especially for terpolymers at composition of VDF/TrFE ratio near or below 50/50mol%. Furthermore, the synthesis parameters for the terpolymer with lower VDF/TrFE ratio are very different from those with higher VDF/TrFE ratio (for example, when using the synthesis parameters of ISL17 to synthesize ISL18, both the resin quality and composition uniformity are not high). We intend to do a synthesis study in the future to understand how the synthesis parameters change with the composition and influence the resin quality.

The purpose of synthesis terpolymers with VDF/TrFE ratio at or below 50/50 mol% is to lower the weak field dielectric constant so that the energy density at high field can surpass those with VDF/TrFE mole ratio higher than that. In deeded, the weak field dielectric constant of ISL18 and ISL19 is lowered (as shown in figure 1 which is a comparison of the dielectric constant between ISL18 and ISL14). Because of poor resin quality, the breakdown field for ISL18 and ISL19 is below 200 MV/m (compared with the other compositions (VDF/TrFE mole ratio higher than 63/37) for which the resin quality is much better and the

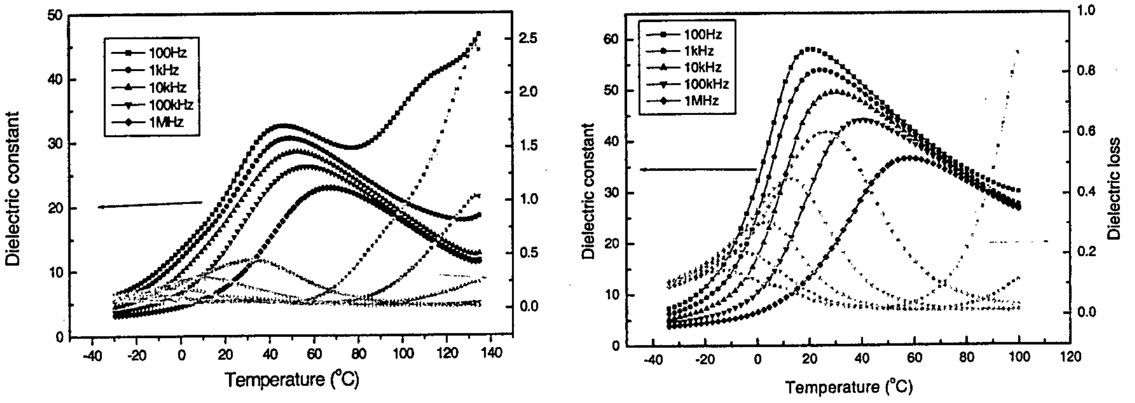


Figure 1. Dielectric constant as a function of temperature for ISL18 (46/54/6.8 mol%) and the terpolymer of 63/37/7.5 mol%. By lowering the VDF/TrFE mole ratio to near or below 50/50 %, the weak field dielectric constant is lowered (along with the loss).

breakdown field can reach above 400 MV/m). However, it is noted that the energy density at lower field for ISL18 and ISL19 is reduced compared with other terpolymer compositions which indicates a reduced polarization saturation effect as intended. Further improvement in the synthesis conditions for the terpolymers in the lower VDF/TrFE mol% will be made in the future so that high dielectric strength can be achieved. (ISL18 also shows a high AC conduction as indicated by the increased low frequency (100 Hz) dielectric constant and loss at temperatures above 70 °C).

2. Terpolymer film fabrication at ECI

Currently, there are 3 batches of terpolymer compositions which have enough resin (>500 grams) to produce films at ECI using their drum cast machine. In the middle of August, 04, ECI has produced films of 15 μm thick of ISL14 (63/37/7.5 mol%) using their drum cast set-up. The films received are shown in figure 2. The total length of the films is 280 feet with the initial 50 feet not usable (for adjusting the cast parameters). A 250watt IR light 6-8" from the film surface moving at 5 feet per minute helped to dry the film a little. The width of the film is 5" and the center 3-4" of film width has good quality throughout (when inspected using optic method). The resin quality of ISL17 does not allow for high quality film to be produced using the drum cast method at ECI. Currently, we are evaluating ISL16 to determine whether it is suitable for drum cast at ECI.

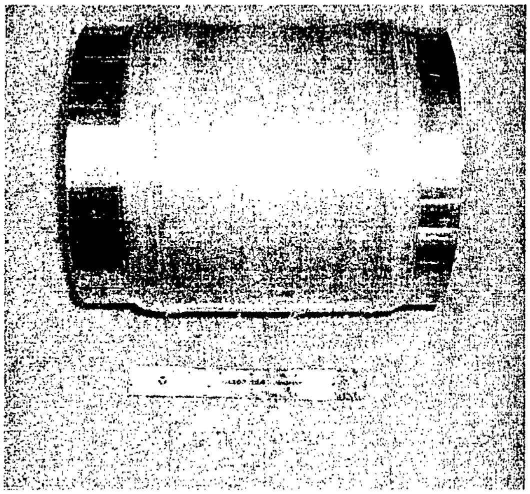


Figure 2. the thin films (280 feet long) of terpolymer 63/37/7.5 mol% fabricated at EC

3. Energy density, DC and AC conductivity, and other related properties

(3.1) Energy density measured from the polarization loop at 10 Hz and AC and DC conductivity

As a non-linear dielectric polymer, the stored and discharged electric energy density should be directly calculated from $U_e = \int E dD$, where D is the surface charge density (electric displacement which is the same as the polarization for the polymers investigated here). Using the polarization hysteresis loop measured under unipolar condition, the stored and discharged energy density can be obtained as schematically shown in figure 3. Figure 3 is for the terpolymer P(VDF-TrFE-CFE) 63/37/7.5 mol% measured at 10 Hz and the shaded area is the discharged energy density. The enclosed

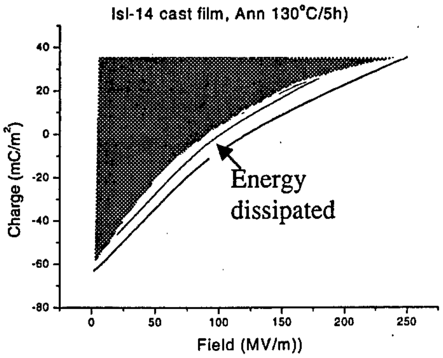


Figure 3. Determination of the discharged (released) energy density (shaded area) and dissipated energy density (open srae).

and unshaded area represents the energy dissipated. The total stored energy density is the summation of the discharged energy density plus the dissipated energy density, from which the efficiency of the dielectric film (or a capacitor) can be determined. In this experiment, the applied field E increases from zero to a maximum value (charging the capacitor) and then is reduced to zero (the capacitor discharge). If there is no conduction loss, the charge density at E=0 at the end of discharging cycle should be the same as that at the beginning of the charging cycle. Due to AC conduction loss, the polarization at E=0 after the charging/discharging cycle does not return to the initial value. Therefore, this difference in the polarization (or charge density) at E=0 between the beginning and ending of the cycle is a measure of AC conductivity in the film (or capacitor). The experimental data show that this AC conductivity is sensitive to the film processing condition (such as the solvent used and annealing condition) and also the stress applied during the measurement in addition to the resin quality. More importantly, the moisture absorbed can greatly increase this AC conduction loss. Figure 4 illustrates how this AC conduction loss depends on the processing conditions for P(VDF-TrFE-CFE) 70/30/8.1 mol% (different solvents, annealing conditions, and applied local stress during the measurement). The data also indicate that in these terpolymers, in addition to the AC conduction, there is also intrinsic dielectric loss owing to the ferroelectric nature of the polymer. We are in the process to (i) evaluate how the AC conductivity of the terpolymer depends on the film processing and measurement conditions and (ii) compare the AC conductivity of the terpolymers with other polymers, especially the commercial P(VDF-TrFE) copolymers. It was found that moisture absorbed by the terpolymer can raise both the AC and DC conductivity quite markedly. It was also found that in some well prepared terpolymer films, the AC conduction can reach the level of the commercial copolymer. How to reduce the intrinsic AC conduction loss and ferroelectric hysteresis loss is an area to be investigated in the future.

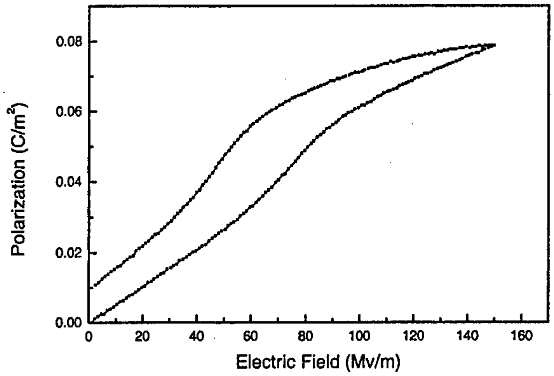


Figure 4. (a)

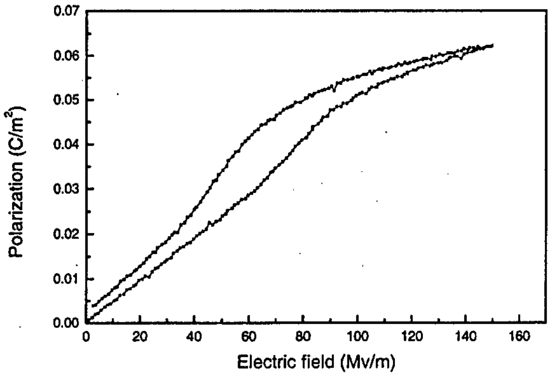


Figure 4. (b)

DC conductivity was also evaluated for several terpolymers (all measured under 100 V) and is summarized in Table 2. As the reference, the DC conductivity of the commercial PVDF copolymers is also included. The commercial PVDF copolymer films were fabricated from the resins obtained using the same solution cast method as that to fabricate the terpolymer films. It seems the DC conductivity of the terpolymers is nearly the same as that of the commercial PVDF copolymers processed under the same conditions. In the future, the commercial copolymer films will be acquired and used for the comparison.

Table 2. DC resistivity of terpolymers as well as comparison with the commercial copolymers

Polymers	DC Resistivity (Ωcm)
Commercial copolymers	
P(VDF-TrFE) 65/35 solution cast (DMF)	1×10^{14}
melt-pressed films	7.1×10^{13}
P(VDF-HFP) 90/10 solution cast (DMF)	7.2×10^{13}
melt-pressed films	1.8×10^{14}
Terpolymers	
ISL14: P(VDF-TrFE-CFE) 63/37/7.5 solution cast DMF	9.9×10^{13}
Solution case MEK	7.9×10^{13}
Melt-pressed films	5.7×10^{13}
ISL17: P(VDF-TrFE-CFE) 70/30/8.1 solution cast DMF	7.8×10^{13}
Solution cast MEK	5.9×10^{13}
Melt-pressed films	4.8×10^{13}

Table 3. The discharged energy density and efficiency from the unipolar polarization loop measurement for the two terpolymers characterized

Composition	Electric Field (MV/m)	Released Energy (J/cm^3)	Consumed Energy (J/cm^3)	Efficiency	Thickness (μm)
ISL-5, gold electrode 65/35/8.5	310	6.03	1.67	0.78	11
	327	6.43	1.87	0.77	11
	345	6.81	2.09	0.76	11
ISL-5, Al electrode 65/35/8.5	310	5.87	2.25	0.72	11
	327	6.24	2.61	0.70	11
	345	6.61	2.94	0.69	11
	360	6.97	3.3	0.68	11
ISL-14 (63/37/7.5 mol%)	314	6.45	2.19	0.74	7
	342	7.23	2.67	0.73	7
	371	8.16	3.16	0.72	7
	400	8.9	3.7	0.71	7

Figure 5 presents the charging and discharging curves of the terpolymer 63/37/7.5 mol% measured at 10 Hz under different applied field level (400 MV/m is the highest field measured). From the data, the discharged energy density and efficiency are determined. For this film, the electric energy density is 8.9 J/cm^3 under 400 MV/m with an efficiency of 71%. The data are summarized in Table 3. In the table, the measured results from ISL5 (65/35/8.5 mol%) are also included. It is noted that the electrodes used also affect the efficiency (mainly through the charge

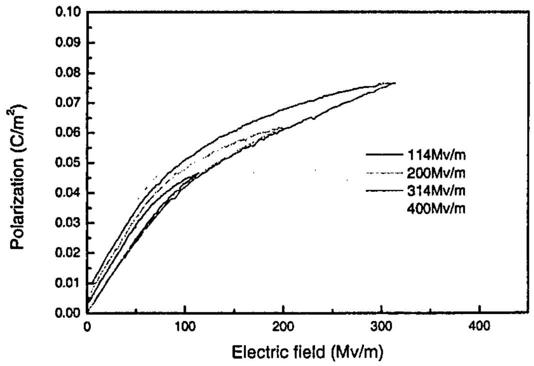


Figure 5.

injection at the interface and hence AC conduction loss).

Figure 6 presents the discharged energy density for 63/37/7.5 nol% measured on two samples (crosses and open circles) and for 68/32/9 mol% which can reach 10 J/cm^3 under 350 MV/m. These results along with the data in Table 2 indicate that both VDF/TrFE ratio as well as CFE mol% will affect the discharge energy density. More characterization over a broad composition range and processing conditions will be needed to establish general guidance on the energy density and efficiency in this class of polymers.

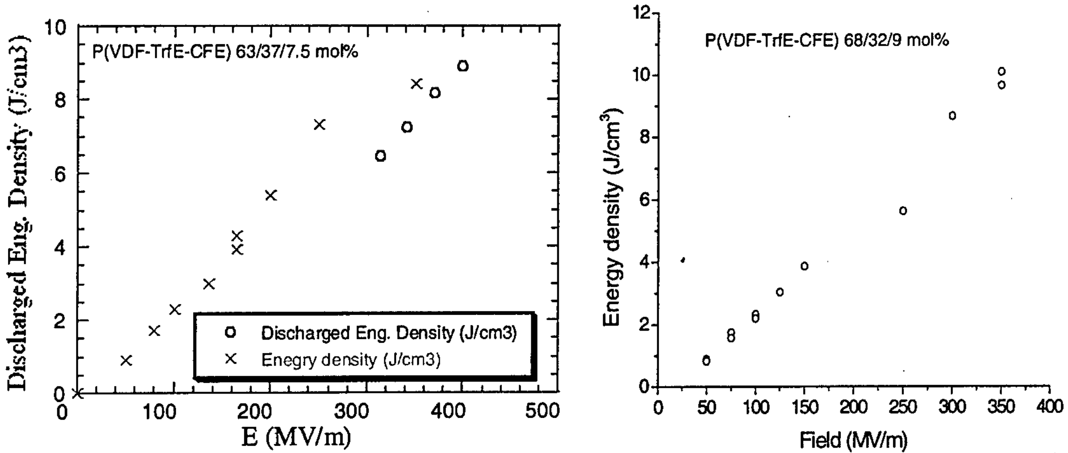


Figure 6. (a)

Figure 6. (b)

(3.2) Pulse discharge measurement of the discharged energy density from the terpolymers

As a first step to measure the high voltage high speed discharge characteristics of these terpolymers, a high speed high voltage amplifier circuit was designed and built. Currently, this circuit can handle voltage up to 2.3 kV with a voltage drop to zero to below 0.2 ms. The schematic of the circuit is shown in figure 7 and this circuit will be improved in the near future so that higher voltage (~10 kV) can be applied in the measurement. We are also in the process of designing and building a circuit with high voltage and high speed capability using IGBT switch to measure the discharged energy density released to a resistive load.

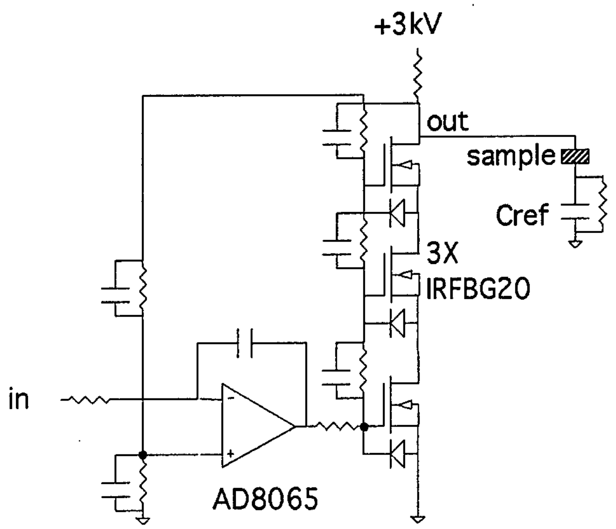


Figure 7.

Using the circuit of figure 7, the discharge energy density for the terpolymers was characterized. In these measurements, the falling time of the voltage pulse is adjusted to 1 ms and the actual measuring time is 1.25 ms. The results from these discharge measurements are summarized in Tables 4 (for the low fields) and Tables 5 and (for the high fields) for the terpolymer of 70/30/8.1 (ISL17) and 63/37/7.5 mol% (ISL14).

Table 4.

Samples	Electric field (MV/m)	Energy (J/cc)	Film Thickness	Electrode Diameter
ISL-17, solution casting unstretched (70/30/8.1 mol%)	109.4	2.12	21 μm	2.46 mm
ISL-17, solution casting stretched (70/30/8.1 mol%)	142.6	2.34	16	2.46
ISL-14 solution casting Unstretched (63/37/7.5 mol%)	138.7	2.632	16	2.46

The highest fields measured for these films were limited by the circuit voltage (2.3 kV). The data indicate that with about 1 ms discharge time and under 320 MV/m, these terpolymer films can reach energy density higher than 6.6 J/cm^3. From the energy density data obtained from the unipolar polarization loops, it is expected that with increased field, this energy density will be increased. For example, figure 6 shows that for the terpolymer 63/37/7.5 mol% under 320 MV/m, the discharged energy density measured at 10 Hz (100 ms) is in the range from 6.7 J/cm3 to 8 J/cm^3. The data in Table 5 (figure 8) show that at 321 MV/m, the discharged energy density for the same terpolymer measured at 1 ms is 6.64 J/cm^3 which is not very much below that from figure 6.

Table 5. Discharge Energy of ISL-14 (63/37/7.5 mol%) Film on Glass Substrate

Electric field (MV/m)	Released Energy (J/cm^3)	Falling time (ms)	Film Thickness (μm)
57.1	0.544	1.25	7
116.1	1.646	1.25	7
171.4	2.892	1.25	7
236.6	4.418	1.25	7
283.5	5.515	1.25	7
321.4	6.647	1.25	7

Table 6. Discharge Energy of ISL-17 (70/30/8.1 mol%) Film on Glass Substrate

Electric field (MV/m)	Released Energy (J/cm^3)	Falling time (ms)	Thickness (μm)
50	0.48	1.25	8
100	1.996	1.25	8
150	3.345	1.25	8
200	4.341	1.25	8
225	4.727	1.25	8
250	5.126	1.25	8

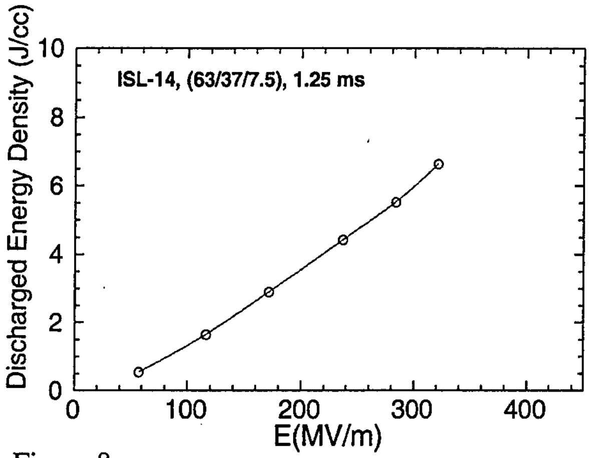


Figure 8

The discharge data for the terpolymer 65/35/8.6 (ISL5) was characterized at room temperatures and 50 °C and at two discharging time, 1.28 ms and 0.64 ms. The data are summarized in Tables 7, 8, and 9. There is not large difference in the discharged energy density between that measured with 1.28 ms discharge time and 0.64 ms discharge time (also see figure 9). Films of two different thicknesses were tested: 3.6 µm and 11 µm and the data seem to indicate that the energy density of 3.6 µm thick films under same electric field is lower than that of 11 µm thick. Further tests will be performed to confirm this. There is no marked difference in the energy density between that measured at room temperature (20 °C) and that at 50 °C under the same field. However, the breakdown field of the films at 50 °C is lower which might be due to the reduced elastic modulus of the terpolymer film with temperature (electromechanical breakdown). Further investigation will be performed.

Table 7 Discharge data for Isl-5 (65/35/8.6% thickness=3.6μm) at room temperature

	Electric field (Mv/m)	Discharge energy (J/cc)	Discharge time (ms)	Thickness (μm)	Diameter (mm)
13Hz	27	0.12	1.28	3.6	2.46
	59	0.47	1.28	3.6	2.46
	90	0.95	1.28	3.6	2.46
	121	1.47	1.28	3.6	2.46
	147	2.06	1.28	3.6	2.46
	190	2.88	1.28	3.6	2.46
	217	3.45	1.28	3.6	2.46
	238	3.93	1.28	3.6	2.46
	258	4.4	1.28	3.6	2.46
26Hz	27	0.11	0.64	3.6	2.46
	59	0.47	0.64	3.6	2.46
	90	0.91	0.64	3.6	2.46
	122	1.47	0.64	3.6	2.46
	152	1.99	0.64	3.6	2.46
	190	2.73	0.64	3.6	2.46
	238	3.73	0.64	3.6	2.46

Table 8 Discharge data of Isl-5 (65/35/8.6%, thickness=11μm) at room temperature

	Electric field (Mv/m)	Discharge energy (J/cc)	Discharge time (ms)	Thickness (μm)	Diameter (mm)
13Hz	45	0.49	1.28	11	2.46
	93	1.43	1.28	11	2.46
	118	1.96	1.28	11	2.46
	138	2.31	1.28	11	2.46
	158	2.77	1.28	11	2.46
	182	3.2	1.28	11	2.46
26Hz	44	0.46	0.64	11	2.46
	86	1.31	0.64	11	2.46
	113	1.8	0.64	11	2.46
	138	2.19	0.64	11	2.46
	155	2.63	0.64	11	2.46
	182	3.21	0.64	11	2.46

Table 9 Discharge data of Isl-5 (65/35/8.6% thickness=11μm) at about 50°C

	Electric field (Mv/m)	Discharge energy (J/cc)	Discharge time (ms)	Thickness (μm)	Diameter (mm)
13Hz	44	0.46	1.28	11	2.46
	77	1.1	1.28	11	2.46
	98	1.61	1.28	11	2.46
	121	2.31	1.28	11	2.46
26Hz	44	0.44	0.64	11	2.46
	76	1.09	0.64	11	2.46
	98	1.61	0.64	11	2.46
	121	2.30	0.64	11	2.46

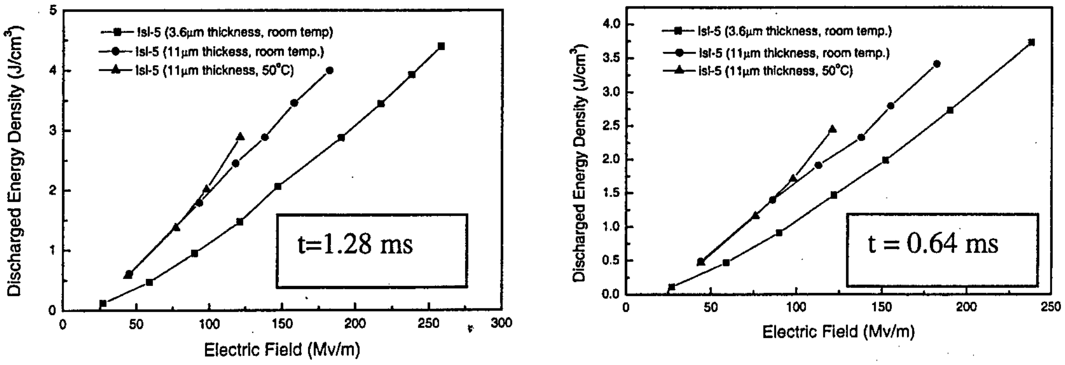


Figure 9. Discharged energy density for ISL5 at different discharge times.

4. Effect of the surface coating of acrylate on the breakdown field — Improved breakdown field

Sigma Lab has reported recently a result on improved breakdown field for the PVDF-TrFE copolymer when a thin layer (less than 1 μm thick) of acrylate film was coated. Uisng the large films fabricated by ECI at New Jersey (ISL 14, 63/37/7.5 mol% terpolymer), Sigma Lab also performed the coating for us. As summarized in Table 10, (the highest field allowed in our set-up is 5,000 volts), the breakdown field of the acrylate coated terpolymer is substantially improved for these films (in thickness from 13 to 18 μm thick). In the last columm of the Table, the film breakdown or not are indicated. As can be seen, for the coated films, many films even at 384 MV/m do not show breakdown. Using a preliminary Weibull analysis, the fitted parameter for the breakdown field E_b for uncoated films is about 350 MV/m while for the coated films, this E_b is above 450 MV/m. The reason for this improvement is not clear to us. It could be due to the composite film structure (a two layered film) or due to the fact that the coated layer (acrylate) fills the pits in the terpolymer films and consequently raises the breakdown field. Further investigation will be conducted along this direction.

Table 10 Breakdown results for Isl-14 and acrylate coated Isl-14 films

Sample name	sample number	Thickness (μm)	Before test		After test		Vo ltage (Volt)	Electric field (Mv/m)	Breakdown or not
			C (pf)	D	C (pf)	D			
Coated Isl-14 films	1	14	813	0.087	836	0.086	2140	152	yes
	2	13	816	0.087	813	0.089	5000	384	no
	3	15	755	0.098	777	0.093	5000	333	no
	4	14	750	0.081	737	0.083	4650	332	yes
	5	14	862	0.085	869	0.086	4900	349	yes
	6	14	2020	0.076	1950	0.077	5000	357	no
	7	13	1990	0.081	1780	0.084	5000	357	no
	8	13	1870	0.075	1880	0.071			
	9	13	2080	0.08	2090	0.083	4900	376	yes
	10	14	950	0.078	801	0.084	5000	357	no
	11	14	769	0.075	768	0.075	4050	289	yes
	12	13	2050	0.088	1960	0.089	5000	384	no
Not coated Isl-14 films	1	15	1930	0.084	1930	0.081	4780	318	yes
	2	14	1789	0.084	1747	0.081	5000	357	yes
	3	16	698	0.077	665	0.079	4250	265	yes
	4	16	627	0.087	640	0.085	5000	312	no
	5	17	669	0.082	688	0.079	5000	294	yes
	6	18	660	0.082	701	0.079	5000	277	no
	7	15	684	0.082	724	0.079	4620	308	yes

The results in Table 10 also list the capacitance and loss for the films before and after the breakdown. It is interesting to note that both no-coated and acrylate coated terpolymer films show graceful failure. That is, there is no electric shorting after the breakdown (see "after test" column which is the capacitance measured after the breakdown). This needs to be further confirmed. Graceful failure is a feature required for Navy power capacitor applications.

5. High voltage discharge circuit for energy density measurement

The circuit in figure 7 served the purpose for a quick start of the program in characterizing discharge energy density of the terpolymers. There are many limitations of that circuit: the voltage allowed by the circuit is low (2.3 kV), the discharge time is limited (>0.5 ms), and the energy density measured by the reference capacitor may not be as accurate as that measured by a resistive load. TRS technologies, Inc. has built a discharge circuit with fast switching time, high voltage operation (8 kV), and direct resistive loading for the discharged energy measurement. This circuit will be discussed in more detail in the part summarized by TRS Technologies, Inc.

Discharge measurement using this new circuit will be carried out in the new ONR program.

6. Some of the works conducted at TRS and Electronic Concepts, Inc. are summarized in the following:

6.1. Terpolymer Solution Casting

TRS and ECI cast two terpolymer resins, ISL-14 and ISL-17 provided by Prof. Zhang and synthesized by Prof. F. Bauer at the Institute of Franco Allemand in Saint-Louis, France. The two resins contain differing PVDF/TrFE ratios and CFE contents. ISL-14 has a high dielectric constant of 50 at 25°C while ISL-17 has a lower permittivity but may possibly store more energy due to a high polarization saturation field.

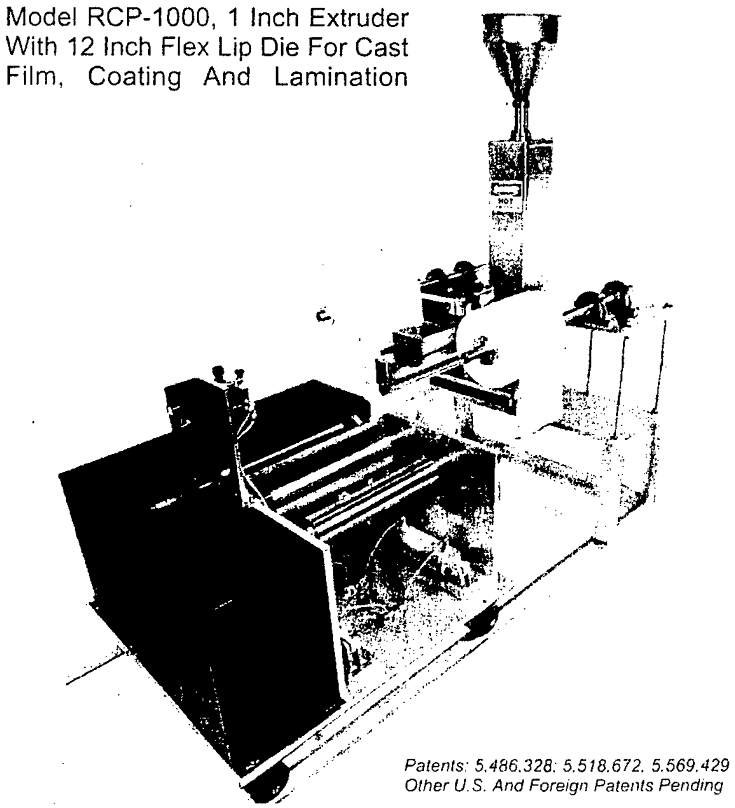
Films of these terpolymers were made by the solution casting method. The resins were dissolved in methyl ethyl ketone (MEK) and cast onto a rotating stainless steel drum. In some cases infrared heaters were used to dry the film before peeling it from the drum using a take-up reel. The terpolymer films were considerably more difficult to cast than conventional PVDF or PVDF-TrFE copolymer. The films plastically deformed very easily and tended to strongly adhere to the casting drum. It was difficult to peel them from the drum without over stretching or even tearing them. These problems were solved by coating the drum with lecithin release agent and using an adjustable motor on the take up reel that allowed one to adjust the tension on the film during casting. IR heating was used on ISL-17 film to help dry it and therefore increase its strength.

The films produced were 15 to 20 μm thick and 12 to 15 cm wide. Subsequent annealing of the film at 120°C for several hours helped to increase elasticity, increase insulation resistance, and reduce dielectric loss. However, in general the film elasticity and strength were probably still too low for good yield and reliability in subsequent metalization and capacitor winding operations. Recommendations for improving film strength for better handle-ability are

1) Fabricate film by extrusion and stretching instead of solvent casting to eliminate residual solvent that could be contributing to low elasticity and strength. Stretching also tends to improve film properties, but could be problematic if inherent film strength is too low.

2) Try to increase degree of cross linking in cast or extruded films to increase elasticity. This may also lead to increased energy density through higher breakdown strength. Cross linking agents would need to be added during casting operations.
3) Use terpolymer compositions with lower CFE content. CFE is a large side group that probably interferes with cross linking leading to low elasticity.

Since the effects of solvent on film strength and elasticity are expected to be detrimental, use of extrusion and stretching is an attractive alternative to solvent casting for fabricating stronger film. This is the method currently used to make BOPP and other high quality polymer films. A major impediment to making extruded and stretched films is the very large amount of resin needed for even pilot scale extrusion equipment (typically in excess of 50 kg). Currently terpolymers are only available in 1 to 2 kg lot sizes. To address this problem TRS did an assessment of small laboratory scale extruding systems. Randcastle Extrusion Systems, Inc. (http://www.randcastle.com/) makes such equipment, and they provide extrusion services and consulting for new materials. Their model #RCP-1000 (see figure 10) can be used to make a 15 to 30cm wide film that is 12 to 25 μm thick. The system can extrude as little as 200g of resin, and it can be fitted with special mixing technology that Randcastle has shown produces higher quality extruded product with fewer defects (pinholes, porosity) than conventional, auger mixing systems. The company also makes small scale pelletizing and blown film equipment. TRS recommends investigating these systems for making solvent free terpolymer films in the second Phase of this program.



Model RCP-1000, 1 Inch Extruder
With 12 Inch Flex Lip Die For Cast
Film, Coating And Lamination

Patents: 5,486,328; 5,518,672, 5,569,429
Other U.S. And Foreign Patents Pending

Figure 10: Microtruder extrusion system from Randcastle.

6.2. Film Properties vs. Processing Conditions

To try to better understand the effect of solvent on film performance the properties of films cast at Penn State in MEK and DMF were compared to films made by melt pressing with no solvent. Films were made using a draw down caster. Samples were electroded with sputtered gold and measured for dielectric constant vs. field (LCR meter with blocking circuit), insulation resistance (two-terminal method using a picoammeter), and polarization vs. field (Sawyer-Tower). All samples were stored and measured in a vacuum desicator.

Results for all the films are shown figures 11 and 12. Dielectric constant varies the most at low field (figure 11), and use of MEK for both ISL-14 and 17 seemed to result in lower dielectric constant. For both materials use of DMF seemed to be equivalent to melt pressing. Resistivity vs. time is shown figure 12. In general the insulation resistances were very good. BOPP has an insulation resistance of 10^{17} Ω-cm and most of the terpolymer samples were over 10^{15}. Melt pressed films of both compositions had equivalent resistivity, but the solvent cast films varied widely. There was no consistency among solvent systems and terpolymer compositions suggesting the variations were perhaps due to the dissolution and casting processes themselves. Film inhomogeneities, defects, or contamination could all be sources of resistivity variations. Nonetheless, the resistivities are very high which is important for reliable pulsed power capacitors.

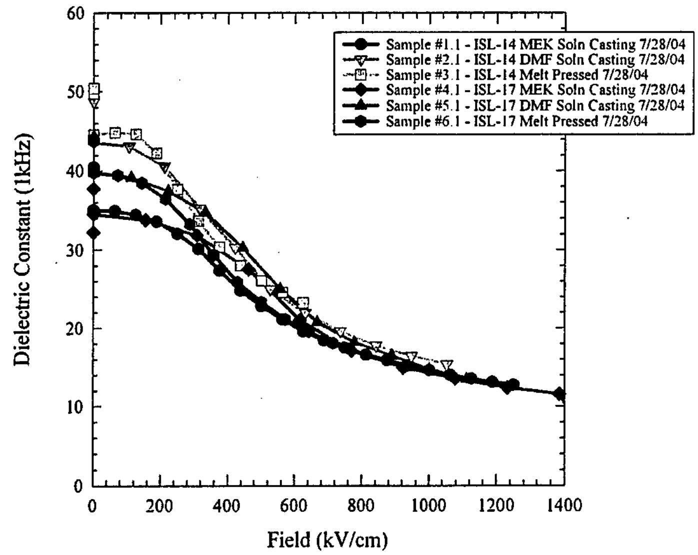


Figure 11: Dielectric constant vs. DC bias field for terpolymer films cast with MEK or DMF or formed by melt pressing.

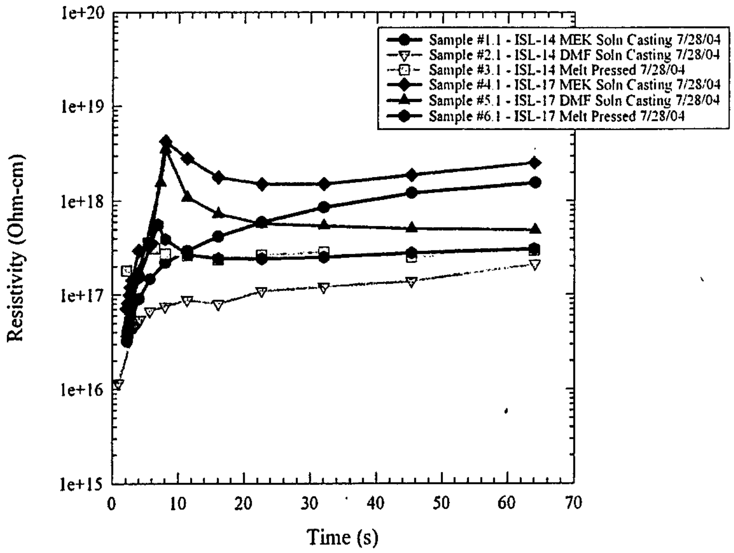


Figure 12: Resistivity vs. time for terpolymer films cast with MEK or DMF or formed by melt pressing.

6.3. Discharge Circuit

To better understand the performance of terpolymer film and composites under conditions similar to the operation of pulsed power capacitors, we have constructed a fast discharge circuit to measure both energy density and discharge speed. A diagram of the circuit is shown in figure 13.

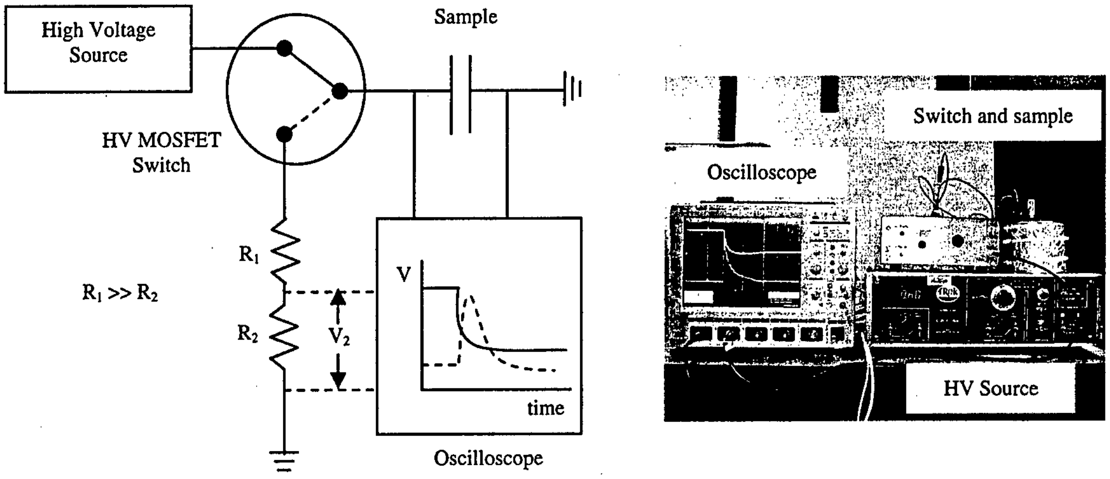


Figure 13: Discharge circuit for measuring energy density and discharge speed of terpolymer and composite films.

A MOSFET is used to rapidly switch between the voltage source (used to charge the sample) and the voltage divider used to determine the change in voltage (and therefore energy) across the sample during discharge. The sample performance during very fast discharge (~ 1 µs) can be determined by using small resistance values in the voltage divider. Use of an MOSFET allows fast discharge without the mechanical oscillations observed in mechanical and mercury switches.

This MOSFET (Behlke HST 80) switch is for high voltage, high speed switching applications. It is rated for 8000V and a peak current of 30 Amps DC. Its switching time is better than 120 ns and leakage current is < 20 μAmp DC.

6.4. Market Potential for High Energy Density Terpolymer Capacitors

The anticipated markets for terpolymer energy storage capacitors are military and medical pulsed power systems such as electromagnetic guns, aircraft launchers (EMALS), and implantable defibrillators. Currently these markets are served by wound polypropylene capacitors (large capacitor banks for pulsed power) and electrolytics (implatable defibrillators). The critical parameter for both these markets is the energy density of the packaged capacitor. Currently the best values for polypropylene are in the 1 to 2 J/cc range while electrolytics are ~ 1 J/cc. Discharge speed is also an important parameter and in general polymers are much better than electrolytics because of the latter's large ESR values.

For volume and weight constrained systems (mobile gun platforms: ships, tanks, and aircraft; implantable medical devices) there is a need to greatly reduce the size and weight of the capacitor banks. Thus, materials such as terpolymer with much higher energy density than polypropylene are important opportunities for reducing capacitor size. This can be seen in Table I a comparison of 1000V capacitors using many different dielectric materials technologies from established commercial suppliers. When a 1000 V capacitor was not available, the parameters were also determined for the appropriate number of capacitors in series to get to 1000V. As can be seen terpolymer capacitors are expected to have considerably higher energy density than any other technology except perhaps AFE ceramics which are known to have reliability problems. They are thus very promising for pulsed power systems. They may also be useful for DC bus capacitors and other power electronics applications, but this will depend primarily on the ESR and AC ripple capability of packaged terpolymer capacitors. These parameters have not yet been measured.

Thus, the most likely market, at this time, for terpolymer capacitors is pulsed power systems. A primary source of funds to commercialize terpolymer film for capacitors will be government technology development programs for large capacitor banks needed in future pulsed power weapons, armor, and launch systems. Considerable development is needed to bring these technologies into the armed services, and capacitors are currently the weakest part of the technology. Capacitors made from terpolymer could dramatically reduce the size of these capacitor banks making pulsed power systems feasible for Navy ships and perhaps even land vehicles and aircraft. Funding levels in the range of \$5 to \$10M are expected to develop large, efficient terpolymer capacitors for this application. The eventual market size is uncertain at this point, but may be in the \$10 to \$20M per year range.

The second source of commercialization funds will be investment to develop pulse power capacitors for implantable defibrillators. Current sales for this application are ~ \$40M per year of 200 μF, electrolytic capacitors specially designed for rapid discharge. These capacitors cost more than \$50 per part due to the high reliability requirements[i]. Thus volumes are probably in the range of 800,000 capacitors per year. Anticipated investment for this market is in the range of \$10 to \$20M. A likely strategy to enter this market would be to license technology to one of the major defibrillator manufacturers and then seek investment from them to commercialize specific products. This limits market share (probably ~ 1/3 of the total market), but mitigates much of the risk in bringing new technology to large, technically difficult market.

The primary requirements needed to commercialize terpolymer film for energy storage capacitors are

1) a source of resin supply in 50 to 100 kg lot sizes
2) stronger, higher elasticity film for reliable would capacitor fabrication
3) development of self healing behavior, perhaps through use of monomer coatings that reduce char formation during arcing.

Completion of these tasks will result in high energy density reliable capacitors suitable for pulsed power systems.

Table I: Comparison of Existing 1000V Power Electronic Capacitor Technology to Terpolymer.

Capacitor	Uses	Capacitance (μF)	Voltage (V)	Size (cm^3)	ESR[*] (mΩ)	Ripple Current (A rms)	Energy Density (J/cm^3)	Volumetric Efficiency (μF/cm^3)	Break Down Strength (V)
Electrolytic[ii]	DC Bus, Pulse Power	1900	500	296	32	15	0.8	6.42	~550
Series Electrolytic	DC Bus, Pulse Power	950	1000	592	64	15	0.8	1.60	~1100
Polymer (BOPP)[iii]	DC Bus, Pulse Power	150	1000	709	15	36	0.10	0.21	~1300
Polymer (BOPP)[iv]	Decoupling, Clamping, Snubber	6.8	1200	282	3	45	0.017	0.02	~1800
Ceramic (X7R)[v]	Decoupling, Filter	45	500	27	3.4	18	<0.2[**]	1.7	~1250
Series X7R	Decoupling, Filter	22.5	1000	54	6.8	18	<0.2[**]	0.8	~2500
Ceramic (COG)[vi]	Snubber, Filter	2.5	500	27	1.1	18	0.01	0.09	~1250
Series COG	Snubber, Filter	1.25	1000	54	2.2	18	0.01	0.02	~2500
Commercial AFE[vii]	Pulse Power, Detonator	0.05[†]	1000	2.4	?	N/A	1.5 – 4.5[†]	0.02 @ 0V	?
Terpolymer	*Pulse Power*	*Assume 150*[††]	*1000*	*~ 33*	*?*	*?*	*~ 3 - 5*[#]	*~ 4.6*	*~ 2000?*

[*] At resonance

[**] Upper limit estimated from $1/2CV^2$, X7R's are nonlinear and have decreasing ε_r with increasing field, thus actual energy density is probably lower than these values.

[†] Capacitance at 0 V; Vendor did not give Specific Energy Density for each Component & Voltage

[††] Assume same design as 150 μF BOPP capacitor.

[#] Assume a film thickness from 10 to 5 μm.

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[i] "Capacitors and the Implantable Defibrillator Market", *Passive Component Industry*, pp. 7-10, Sep./Oct., 2001.

[ii] Cornell Dubilier, Part #450C-192-M-500-BF-0, http://www.cornell-dubilier.com/

[iii] Electronic Concepts, Part #UL30BL0150, http://www.ecicaps.com/ECI_products.htm

[iv] Electronic Concepts, Part #MP80-L685, http://www.ecicaps.com/ECI_products.htm

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[v] AVX, Part #SM0-6-7-C-456-M-A-N-650, http://www.avxcorp.com/docs/masterpubs/Advprod.pdf

[vi] AVX, Part #SM0-6-7-A-255-K-A-N-650, http://www.avxcorp.com/docs/masterpubs/Advprod.pdf

[vii] Novacap, Part #7565-P-544-102-N, http://www.novacap.com/Pulse_Power.pdf