New Polymer Dielectric For High Energy Density Film Capacitors

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Abstract

A new dielectric film has been developed that greatly increases the energy density capability of plastic film capacitors. This film has been developed over the past four years by a consortium consisting of Lithium Power Technologies, Aerovox Corp., Dupont Teijin Films (DTF), Case Western Reserve University, and Ohio Aerospace Institute in an Advanced Technology Program funded by the Department of Commerce. We are now entering the commercialization stage of this project.

Plastic film capacitors have been the capacitor of choice for many power electronics, power conditioning, and pulse power applications such as motors, lighting and portable defibrillators because of their low dissipation factor (DF), excellent high-frequency response, high insulation resistance (IR), self-healing ability, and high-voltage capabilities. Existing capacitor technologies now present a barrier to achieving significant packaging (size and weight) reductions and struggle to meet new market-driven performance requirements. These markets not only include hybrid electric vehicles, wind power and portable defibrillators, but also the military and aerospace markets where the power source must be incredibly lightweight.

Ultra thin gauge biaxially oriented films produced by DTF in thicknesses of 1.4 to 4 microns and thicker were constructed into metallized capacitors ranging from 1 to 140 microFarads. The new dielectric film demonstrated the following compared to PET (polyethylene phtherepthalate) film:

- Gain in dielectric strength of over 30-40%
- At least an order of magnitude increase in insulation resistance
- Enhancement in dielectric constant

These metallized film capacitors, which use either a solid or environmentally benign vegetable oil (dry) fill, can now replace capacitors that use environmentally problematic liquid electrolyte systems. The technology is a promising candidate for the development of a higher energy density, high voltage film capacitors for a large number of applications including, defense, aerospace, defibrillator, automotive, and electric power generation.

Introduction

Polymeric film has several attributes that make it advantageous to use instead of inorganic materials because of their greater efficiency in power conversion. This is manifested by low ESR (equivalent series resistance) and low DF (dissipation factor) as well as intrinsic high voltage capability in capacitor dielectrics made from plastic film. These attributes are critical to applications where power losses must be minimized, such as power electronics and power conditioning, and pulse power applications. Film capacitors have virtually no capacitance coefficient with applied voltage, and metallic migration or leaching does not occur as observed in ceramic capacitors. The film molecule is stable over long-term use and is not prone to dielectric dissipation factor degradation or metallic shorting mechanism.

Capacitors have not kept pace with the rapid advance in solid-state switching devices leading to a lowering of system efficiency while adding significant volume and weight to power electronics systems. The capacitors are typically used in pulse forming networks (PFNs) or Marx generators for the conversion of available prime electrical energy into the necessary short and very fast pulses of energy in the megajoule range. This need becomes even more crucial for space borne applications where the power source must also be incredibly lightweight. **Table 1** shows the performance of state-of-the-art advanced capacitor systems.

Table 1. Performance of advanced capacitor systems.

Capacitor System	J/cc		Operating Temperature (^{o}C)	Rep-Rate (Hz)
	Now	Future		
Polymer film	1	10	125	10^5
Ceramic	0.1-0.5	10	>200	10^5
Electrolytic	1.5-2.5	4-5	60	10^2
Mica	0.2—0.5		>300	$>10^6$

Metallized film capacitors offer exceedingly high power and cycle life, can operate at extremes of temperatures, but lack the energy density of electrolytic capacitors, which cannot be used at very high voltages or at high-rep rate. Ceramic capacitors based on barium titanate,, lead zirconium titanate or lanthanum modified lead zirconium titanate, on the other hand, offer very high dielectric constants (in the hundreds to over 1000) and technically high breakdown voltages in intrinsic samples leading to theoretical energy densities of 100-500 J/cc or about 25-10 J/g. However, these breakdown voltages have not materialized in full-size multi-layer monolithic capacitors and such capacitors only deliver practical energy densities of about 0.1-1 J/cc. A single defect kills a ceramic capacitor.

High voltage pulse power technologies for use in Department of Defense applications such as armor/anti-armor; electromagnetic/electrothermal guns; mine/countermine; air surface and subsurface systems; high power microwave weapons, etc. are usually satisfied today by film capacitor technologies. Commercial applications extend to a.c. motors, lighting, and automotive and implantable and portable defibrillators, among others. For years, government contractors have been developing large banks of film capacitors for various ultra high voltage applications in the kilovolt to megavolt range such as the electrothermal gun driver for use in ship self-defense and surface fire support missions (NSWC); Nova laser system (LLNL); Lab Micro Fusion Facility at Sandia; and numerous other extremely high energy applications [1,2,3]. These pulse power devices have energy storage usually in the 50 Kilo Joules (kJ) to greater than 30 Mega Joules (MJ) range. Some of the newer applications for these capacitors in the military now appear to be land-based rail guns and land-based electromagnetic guns as opposed to satellite-based systems.

Film capacitors based on polypropylene (PP) and polyester (PET) have the ability to operate at very high voltages and with good reliability. They also offer high breakdown voltages, inherent low losses, excellent frequency response, low dissipation factor (DF), and good self-healing abilities. Unlike most other circuit components, existing capacitor technologies now present a barrier to achieving significant packaging (size and weight) reductions and struggling to meet market-driven performance requirements. The energy density of commercial film capacitors is less than 1 J/cc. Polyvinylidene fluoride (PVDF) has a much higher dielectric constant (12) than commercial films such as polypropylene (PP) (2.5) and a practical energy density of about 2.4 J/cc. However, it has a number of drawbacks including non-linearity of the dielectric constant with voltage, very poor insulation resistance, poor clearing or self-healing ability, poor dissipation factor (DF), higher leakage currents, relatively lower breakdown voltages and is very costly.

Table 2 describes some of the common film dielectrics in use today and **Table 3** describes the variation in dielectric constant with frequency. Despite the widespread use of polymer film capacitors in a large number of applications, this capacitor technology has not seen any major energy improvements over the past 40 years.

Table 2. Typical properties of some common types of capacitors.

Capacitor Types	K	Dielectric Strength (V/mm)	DF (%)	Volume Resistivity (Ohms.cm)	Max. Oper. Temp (^{o}C)	Energy Density (J/cc) Intrinsic	Practical	Energy Density % of Intrinsic
Plastic Film								
Polycarbonate (PC)	2.8	350	<1	2×10^{17}	150	3.6	0.5 - 1	28
Polypropylene (PP)	2.2	500	<0.1	1×10^{18}	105	4.1	1 - 1.5	36
Polyester (PET)	3.3	400	<1.5	1×10^{17}	125	4.9	1 - 1.5	30
Polyvinylidenefluoride (PVDF)	12	200	1-5	1×10^{15}	105	19.1	2.4	12
Polyethylenenapthalate (PEN)	3.2	440	<1	1×10^{17}	137	4.4	1 - 1.5	34
Polyphenylenesulfide (PPS)	3.0	360	<0.2	5×10^{17}	200	4.1	1 - 1.5	36

Polyethylene terphthalate (polyester or PET) offers a reasonable dielectric constant, has a higher operating temperature of 125 ^{o}C, and is available in film thickness of less than one micron. However, PET has relatively higher DF with increasing temperature and frequency. For high rep-rate, PET is unsuitable for high pulse power applications.

Polypropylene (PP) has inherently low losses, excellent frequency response and very low DF and ESR with temperature and frequency. In fact, the material possesses a negative temperature coefficient of dissipation factor. The PP chain molecules do not possess polar groups, which are oriented under the effect of electric fields. It is this phenomenon which gives rise to the above beneficial properties. It has the highest breakdown voltage of any capacitor film material. Its only negative may be its maximum operating temperature of 105 ^{o}C.

Devices made with polyethylene naphthalate (PEN), polycarbonate (PC), polyphenylene sulfide (PPS) and polyimide (PI) dielectrics also have extremely stable characteristics over extremes of voltage, temperature and frequency. Although the intrinsic voltage breakdown for most of these film dielectrics are quite high, in full wound capacitors they are usually derated by a factor of 6 to 8 for improved cycle life and reliability.

Table 3. Dielectric constant vs frequency for some common types of capacitors.

Capacitor Type	Dielectric Constant				
Frequency (Hz) →	**100**	**1,000**	**10,000**	**100,000**	**1,000,000**
Polycarbonate (PC)	2.8	2.8	2.7	2.7	2.7
Polypropylene (PP)	2.2	2.2	2.2	2.2	2.2
Polyester (PET)	3.3	3.3	3.2	3.2	3.2
Polyvinylidenefluoride (PVDF)	12.0	11.0	10.2	9.6	7.0
Polyethylenenapthalate (PEN)	3.2	3.1	3.0	3.0	3.0
Polyphenylenesulfide (PPS)	3.0	3.0	3.0	3.0	3.0
Polyimide (PI)	3.5	3.5	3.5	3.5	3.5

An interesting dielectric material that has received some attention in the past two decades is polyvinylidene fluoride (PVDF). This polar polymer exhibits a large dielectric constant (~12) and demonstrates excellent piezoelectric and

pyroelectric properties [4]. PVDF is a partially crystalline linear polymer with a carbon backbone in which each monomer $\{CH_2\text{-}CF_2\text{-}\}$ unit has two dipole moments, one associated with CF_2 and the other with CH_2. In the crystalline phase, PVDF exhibits a variety of molecular conformations and crystal structures depending on the method of preparation. The extruded or cast material usually contains 40 and 60% crystalline material in one or both of the principal crystalline phases, alpha and beta. The alpha phase predominates in material cast from the melt. This phase is converted to beta phase by mechanical deformation of the material at temperatures less than 100 ^{o}C. In commercial production, PVDF film is extruded and mechanically stretched both parallel and perpendicular to the direction of extrusion as are most of the capacitor grade film dielectrics. This causes a preferred orientation of the polymer chains in the plane of the film and also converts a large percentage of crystallites to beta form. It is this biaxially oriented film material which, after polarization forms the basis of piezoelectric and pyroelectric devices. The practical energy density of PVDF-based film capacitors has been about 2.4 J/cc.

Despite its very high dielectric constant, PVDF suffers from a number of problems including, non-linearity of capacitance with voltage, very poor insulation resistance, poor clearing or self-healing ability (resulting in catastrophic failures), higher leakage currents, relatively lower voltage breakdowns, relatively poorer mechanical properties, and the material is not available in uniform thickness and in thin gauge and is quite costly. Table 3 indicates that most of the common capacitor materials exhibit a stable dielectric constant with frequency except PVDF. The performance of PVDF is even worse at elevated temperatures and the application of voltage produces a larger number of clearing sites than at room temperature. PVDF does offer good voltage reversal capabilities without affecting its performance. On the other hand, PP has a poor dielectric constant limiting its overall energy density, but otherwise is an excellent dielectric insulator.

Metallized film capacitors offer the highest volumetric and gravimetric energy densities and reliability of all designs of film capacitors and offer higher pulse power capabilities than foil or other designs. The thin metal layer is capable of vaporizing away if a short or a weak location occurs in the dielectric somewhere. This condition is known as self-healing or clearing phenomenon. In poorer clearing materials, such as those with oxygen deficient materials, carbon accumulates at the clearing site resulting in catastrophic failure as a result of conductive shorts. Clearing should only result in metal oxide insulator formation. Fluid impregnated film capacitors have a very narrow operating temperature range while the metallized version can operate up to 100 ^{o}C with the exception of polyphenylene sulfide and polyimide that can reach an operating temperature range of 300 ^{o}C. Plastic film capacitors can be tailored for very high voltages simply by adjusting the film or dielectric thickness.

Recently, there have been some interests in two laboratories (Steinerfilm, Williamstown, MA and Sigma Labs, Tucson, AZ) in coating a polymer film dielectric with an acrylate material before metallizing to help increase the breakdown voltage and improve the clearing ability of the polymer film. Initial data on polyester film suggest an improvement in the breakdown voltage of the film by about 10-20%. The initial idea behind this was to provide extra oxygen on the polymer dielectric for more efficient burning and hence, improved clearing. It was thought that PVDF would benefit from this coating through enhancement of it breakdown properties [5]. However, numerous testings on PVDF film capacitors made with acrylate coatings do not provide any further improvement to the energy density or breakdown voltages [6]. Furthermore, this theory also breaks down for polypropylene that has no oxygen in its structure and yet exhibits the best clearing ability of all capacitor film material available today. It is now believed by a number of film capacitor companies that the acrylate improves the energy density because the dielectric constant for the acrylate is considerably higher than the polyester material, and has nothing to do with the extra source of oxygen.

Other developments include the use of a uniformly graded metallization process allowing higher resistivity on the body of the film with thicker metallized edges. This design allows further improvements in the breakdown voltages and clearing. Initial results on 5 micron homopolymer PVDF film with such metallization indicates a 30-40% improvement in the breakdown of fully wound film capacitors [6]. Other companies have also developed novel metallization technologies to achieve the same results [7-8].

Presently, there are no film dielectric materials with significantly enhanced energy density over state-of-the-art film capacitors. Future power source systems require significant improvements in capacitor technologies in the efficiency, energy density, reliability, and overall performance over the existing state-of-the-art. It is clear that materials such as those based on homopolymer PET, PVDF or PP, or any other standard dielectric polymer film alone cannot meet these goals.

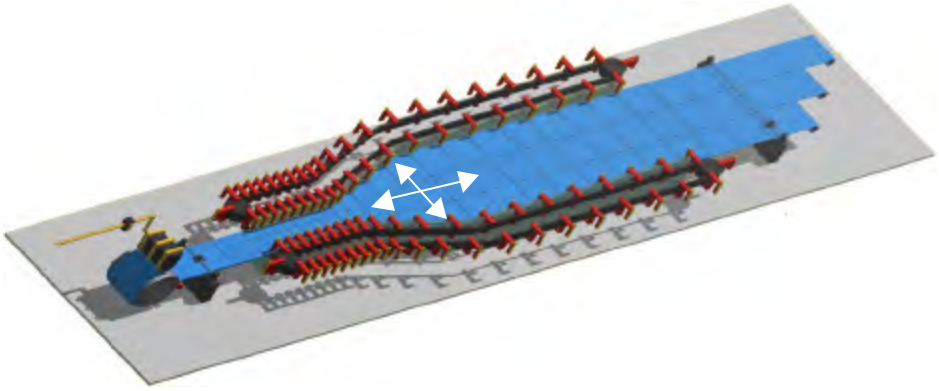
A new capacitor film with higher dielectric constant, higher voltage stability, low dissipation factor, and lower cost would enable significant share gain versus other capacitor types. Lower cost small film capacitors could be manufactured to compete against MLC's in the upper part of the traditional MLC capacitance range. High value film capacitors would compete very effectively versus tantalum or aluminum electrolytic capacitors, based on their superior electrical properties.

In a recent Advanced Technology Program funded by the Department of Commerce, a consortium comprised of Lithium Power Technologies, Dupont-Teijin Films (DTF), Aerovox Corporation, Ohio Aerospace Institute and Case Western Reserve University, a new dielectric polymer film material based on a modified polyethylene terephthalate polyester was developed with significantly enhanced energy density and electrical properties. This paper describes the properties of such a dielectric material in metallized film capacitors.

Experimental

Film Production

The new dielectric film was produced by Dupont-Teijin Films in Luxembourg. The technology of simultaneous stretching technology by means of linear motors was developped by DuPont and has been licensed to Brückner Maschinenbau (Germany Siegsdorf). Brückner commercialized the technology based on latest hardware developments under the tradename of LISIM (r) since 1996. (**Figure 1**).



The LISIM® technology can reliably produce at high speed polyester films in roll up sheet forms down to 0.5 micron thickness. The clips are motorized by linear motors (**Figure 2**) in order to perform the longitudinal stretching (MD) by accelerations while the V-shape induces the transversal stretching. (TD).

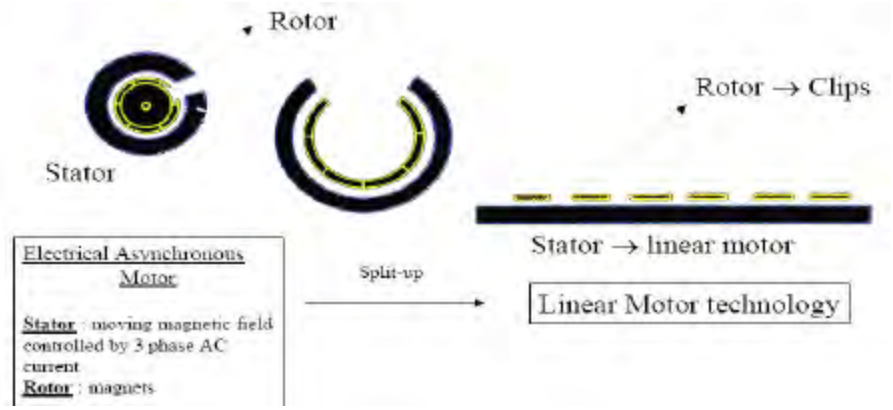


Figure 2: Linear motor technology.

The new modified polyester films (termed HED) in nominal thicknesses of 2.80 µm and 4.24 µm were produced and

their performance in metallized film capacitors compared to baseline PET of nominal thicknesses 3.35 µm and 3.53 µm, respectively.

Film Metallization and Winding

The slit-rolls were metallized in accordance with Aerovox specifications for metallized film used in high energy density light duty pulse capacitors. The main electrode is high resistivity vapor deposited aluminum with a heavier metallization at the contact edge of the film. For a metallized film slit width of 50mm, the film offset plus metallization margins result in an active width of 41mm when two matched pairs of metallized films are wound together to make a capacitor section.

Breakdown Voltage Measurements on Plain Film

The setup used to measure the breakdown voltage of film dielectrics consists of a top electrode made of stainless steel ball of diameter 2 mm (actual surface contact of this electrode with the film is a point contact) and a bottom 12 mm diameter lapped and polished stainless steel base electrode. The film is placed between the two electrodes. The two electrodes are connected via alligator clips to a Rod-L Hi-Pot 5000 V power supply. For the breakdown measurements, plain, un-metallized films were used. The voltage was stepped up in 50V increments until a break in the film occurred. Between each sample, the surface of each electrode was gently cleaned of any carbon residue with isopropyl alcohol and alumina polish.

Capacitor Fabrication

The high resistivity metallized films were wound into sections to be built into plastic case dry capacitors. The contact edges of the film at each end of the capacitor sections are connected together and to the terminal leads with zinc endspray. Section teardowns were performed on a few capacitors from each group, to obtain active length and actual thickness based on weights and specific gravity of Mylar® PET (1.395) and and Mylar® HED films (1.41) in the windings. Section teardown results are summarized in **Table 4** (active width 4.1 cm for all four groups):

Table 4. Actual film thicknesses for each of 4 sets of samples.

	"3 mm" control Mylar® PET (WO 279132)	**"3 mm" Mylar® HED (WO 279133)**
Avg.Capacitance, DF (120Hz)	63 µF, 0.6%	70 µF, 0.7%
Active Length	9492 cm	8710 cm
Thickness	3.35 micron	2.80 micron
	"4 mm" control Mylar® PET (WO 279277)	**"4 mm" Mylar® PET HED (WO 279279)**
Average Capacitance	40 µF, 0.5%	39 µF, 0.6%
Active Length	6137 cm	6017 cm
Thickness	3.53 micron	4.24 micron

All four groups of capacitors were built into the same case size with flying leads, as shown below in **Figure 3.**

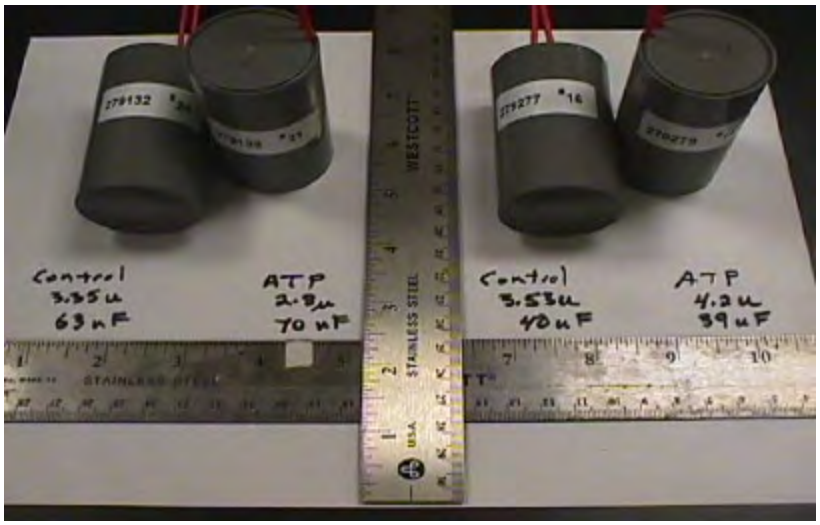


Figure 3. One capacitor from each group, high resistivity metallization on 3 μm and 4 μm (nominal) control Mylar® PET and Mylar® HED (ATP) films.

Results and Discussions

Figure 4 shows the variation in the breakdown voltage of the plain films from sample to sample. As seen in the figure, the breakdown voltages of the Mylar® HED films were on average 100-125 V/μm higher in value than the baseline Mylar® PET films.

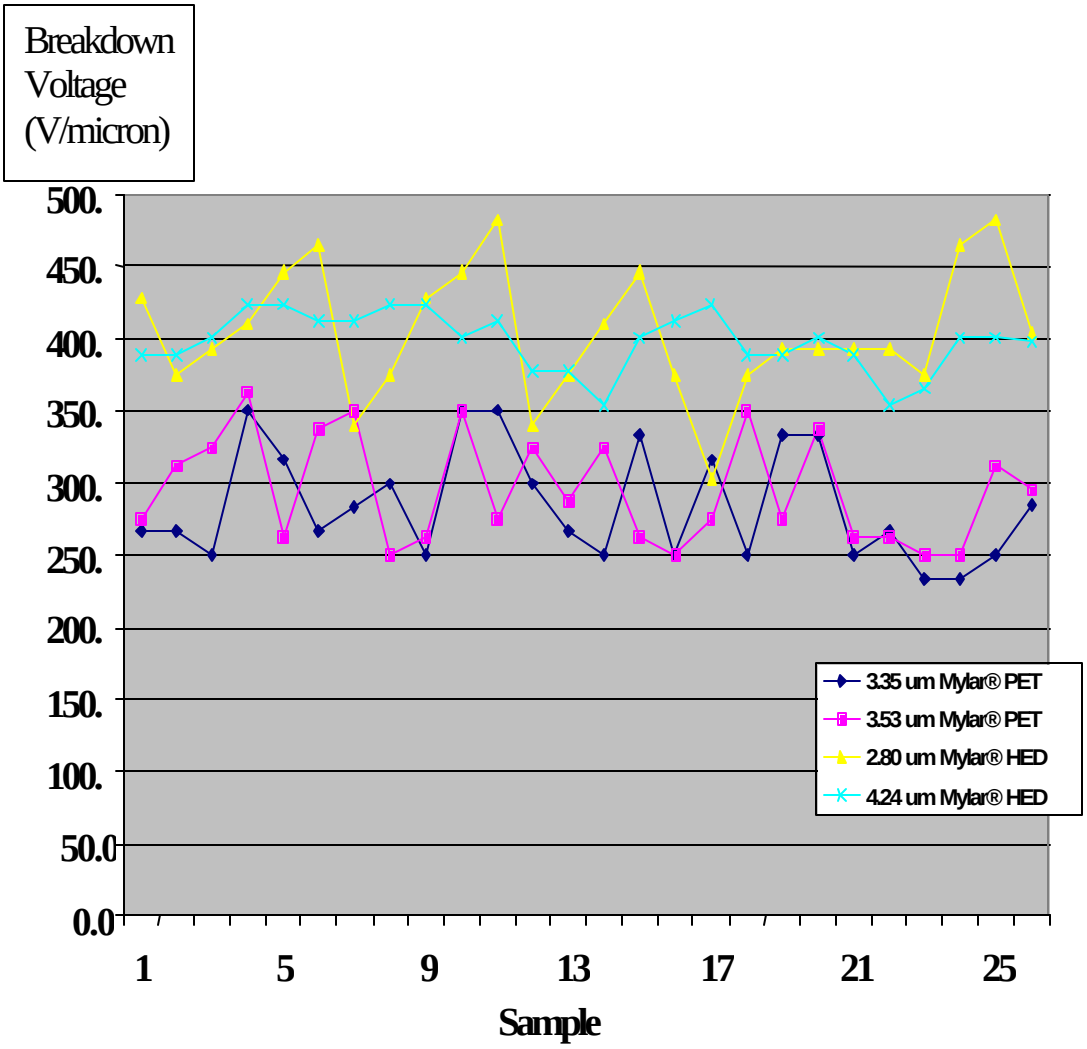


Figure 4. Breakdown voltage variation for 2.80 mm and 4.24 mm Mylar® HED films compared to 3.35 mm and 3.53 mm Mylar® PET films.

Step-up voltage testing was performed on 3 pieces from each group. Cap and DF is measured, a test voltage is held for 1 minute and recorded at the end of one minute, then each capacitor is allowed to self-discharge for 10 seconds and the voltage is recorded at the end of 10 seconds. This sequence is repeated at 100VDC higher voltage than the previous test until massive cap loss and/or the capacitor is unable to maintain the voltage due to run-away leakage current. For both the control and Mylar® HED film capacitors, capacitance remained stable (<1% cap loss) until above 340 – 350 V/μm. The most telling difference between the control and Mylar® HED films is that the Mylar® HED film capacitors can hold a much higher stress than the control capacitors for the same amount of voltage decay from self-discharge. 10 second Voltage decay verses voltage stress for each of the four groups is shown below in **Figure 5.**

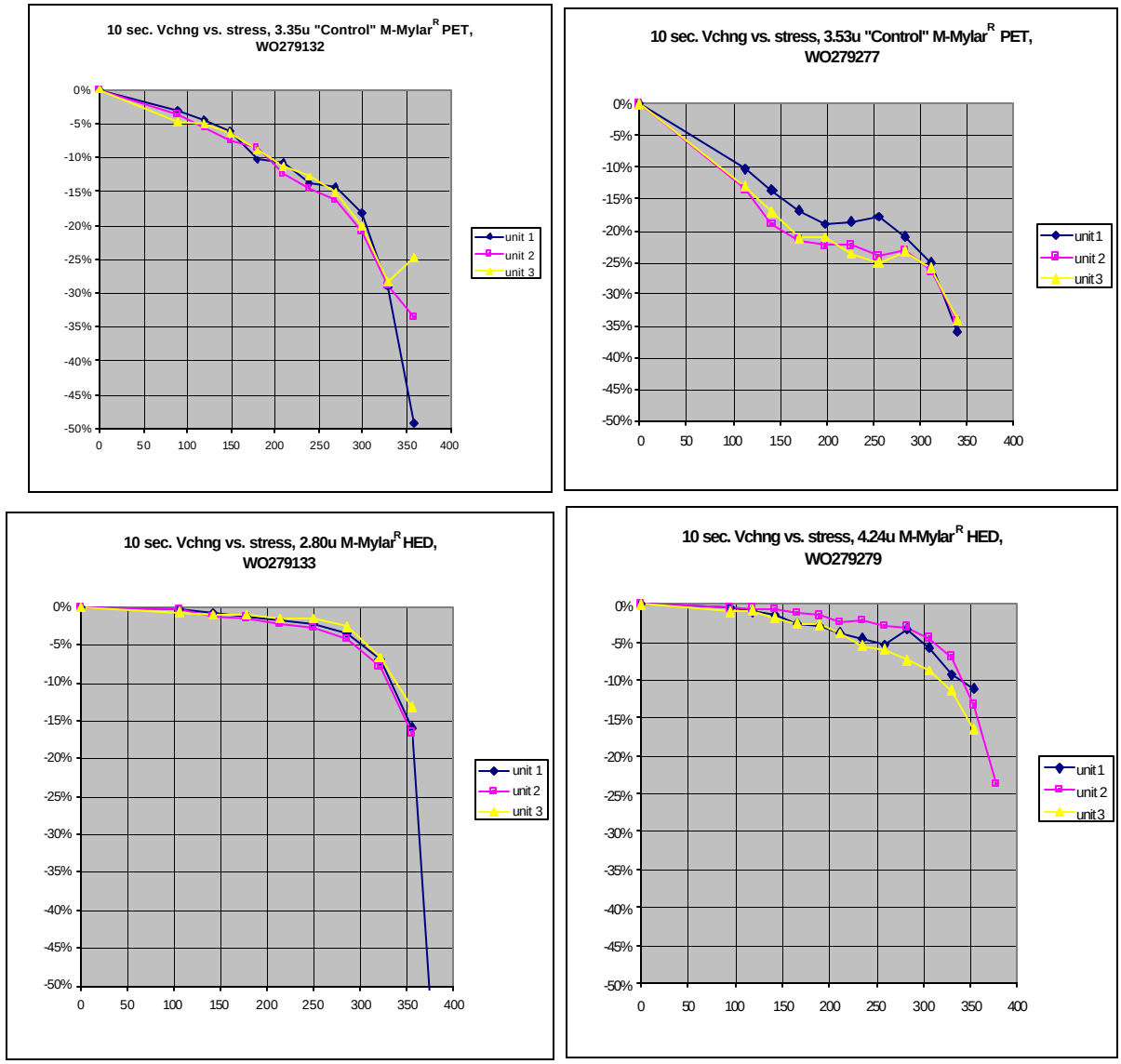


Figure 5. 10 second Voltage drop verses stress, control M-Mylar® PET and M-Mylar® HED capacitors.

Figure 6 shows the capacitance loss as a function of voltage stress for the 3µ Mylar® HED and 3µ Mylar® PET series capacitors. Typically, a capacitor can be stressed until a capacitance loss of 2% of the original capacitance has resulted. While the 3µ Mylar® PET group capacitors are able to withstand voltage stress levels between 300-325 V/µm before losing about 2% capacitance loss, the 3µ Mylar® HED group capacitors perform exceptionally well withstanding voltage stress levels of 425-450 V/µm. This is a 40% improvement in dielectric strength for the 3µ Mylar® HED film capacitors over baseline 3µ Mylar® PET film capacitors.

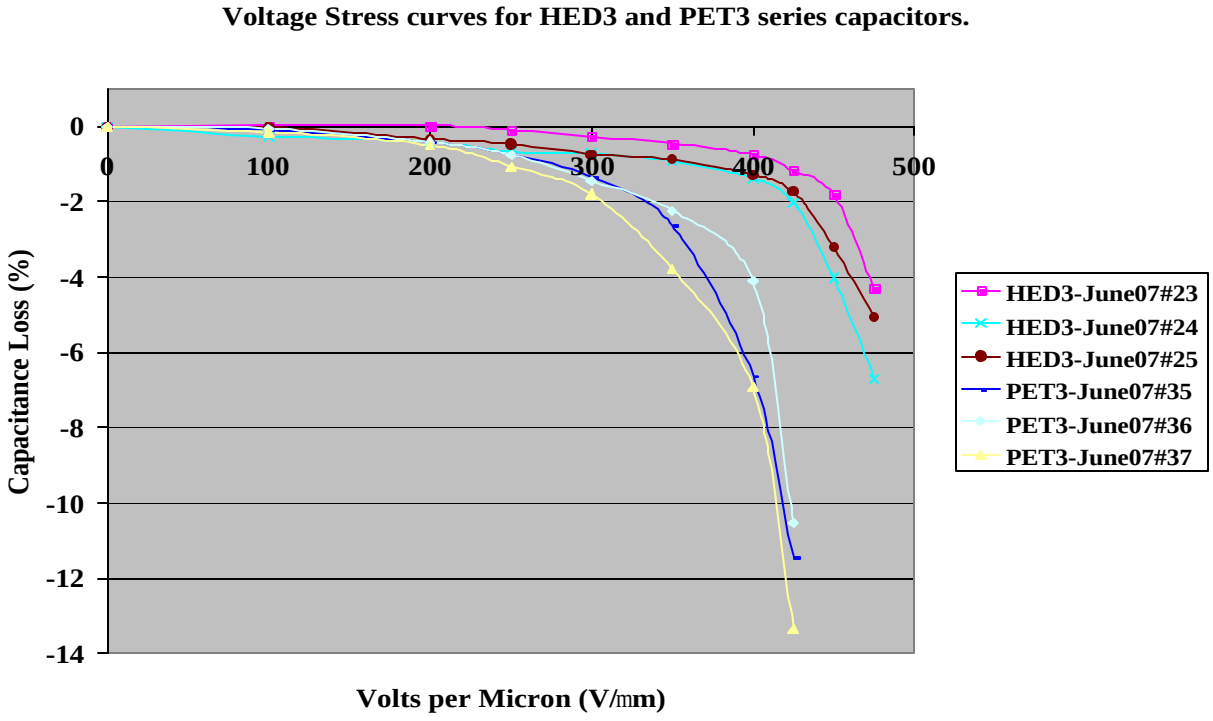


Figure 6. Capacitance loss as a function of voltage stress at room temperature for HED3 (3m Mylar® HED)and PET3 (3m Mylar® PET) capacitors.

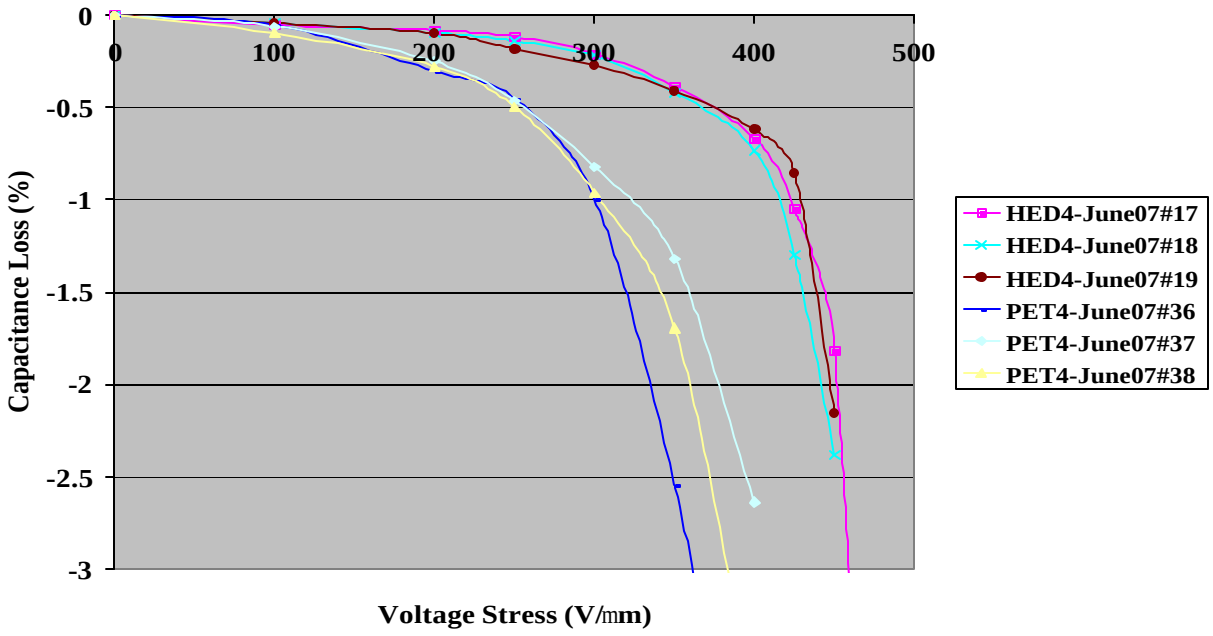


Figure 7. Capacitance loss as a function of voltage stress at room temperature for 4m Mylar® HED4 (4m Mylar® HED) and PET4 (4m Mylar® PET) capacitors.

Figure 7 shows the capacitance loss as a function of voltage stress for the HED4 (4µ Mylar® HED) and PET4 (4µ Mylar® PET) capacitors. The PET4 group capacitors with slightly thicker films appear to yield slightly higher voltage stress than the PET3 group capacitors. Voltage stress levels of 300-350 V/µm could be obtained. However, even the HED4 group capacitors were able to withstand higher voltage stress levels of between 400-450 V/µm.

Pulse testing was performed by charging each capacitor to a test voltage, discharging through a 50 ohm resistor, and repeating the cycle two times per minute. For each group, 3 pieces were tested at a given voltage until capacitance loss was in excess of 10%. End of life was considered to be 5% capacitance loss, or the capacitor going into thermal runaway. Several 3 piece groups were tested at different voltages, in order to obtain pulse life data at stresses ranging from ~240 to 360 V/µm. for 10,000 shots to 5% cap loss.

As shown in a plot of pulse life verses stress in Figure 8, for a lifetime of 10,000 pulses, the Mylar® HED film capacitors could operate at 280V/µm while the control would be restricted to 240 V/µm, and for a lifetime of 1000 shots, the Mylar® HED capacitor could operate at 310 V/µm verses 270 V/µm for the control M-PET capacitors. This is a 35% increase in energy density capability for the same life for the new Mylar® HED film dielectrics.

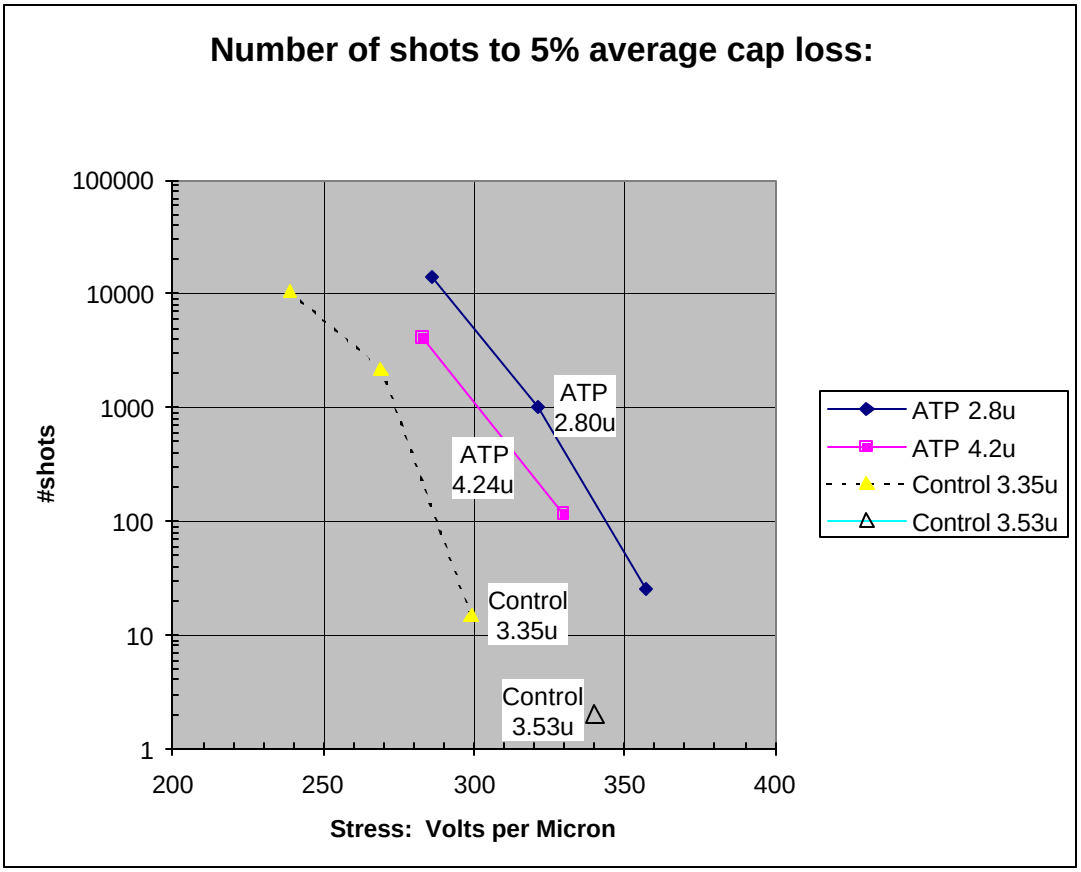


Figure 8. Pulse life verses stress for Control (M-Mylar® PET) verses ATP (M-Mylar® HED) film capacitors.

Conclusions

The Mylar® HED film has demonstrated voltage capability 30 to 40% higher than Mylar® PET film of the same thickness for both held voltage and charge-discharge cycle lifetime. This translates to a potential reduction of almost a factor of two in size for a film capacitor in the same DC or pulse type application requirement using this new film. Since pulse life is a very steep function of stress, this also means that an Mylar® HED film capacitor will have an operational life time more than 10 times as great as a Mylar® PET film capacitor of the same size. The factor of 3 to 10 decrease in self discharge voltage drop (which equates to a factor of 3 to 10 increase in insulation

resistance) translates into a factor of 3 to 10 decrease in power loss during sustained DC voltage operation of the Mylar® HED film capacitor compared with the same size Mylar® PET capacitor.

These metallized Mylar® HED film capacitors, because of their greatly increased energy density over currently available metallized film capacitors, can now replace electrolytic capacitors in the 300 to 1200V range that use environmentally problematic liquid systems. These Mylar® HED film capacitors use either use a solid or environmentally benign vegetable oil (dry) fill, and have benign failure modes, such as capacitance loss, while electrolytic capacitors can explode upon failure.

Acknowledgements

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References

1. NASA Contract NASA-25800 Report, "High-Power Converters for Space Applications" June 1991.
2. D. Strachan, R.Ford, J. Hammon, T. DaSilva, F. MacDougall and T. Weise, "Design and Performance of a Transportable 1 MJ Pulsed Power Source for Electric Gun Investigation" Pres. At the 9th IEEE Pulsed Power Conf., Albuquerque,NM June 22, 1993.
3. L.X. Schneider, S. R. Babcock and G.E. Laderach, "Lifetime Testing of Commercially Available 3.0 mF, 100 kV Pulsed-Power Capacitors", 7th IEEE Pulsed Power Conf., Monterey, CA, 1989.
4. H. R. Gallantree and R. M. Quilliam, in: "The Marconi Review" Fourth Quarter, 1976, p 189.
5. Dick Wooden, ASC Capacitors, private communications, (1997).
6. M. Z. A. Munshi, internal testing of PVDF capacitors at Sulzer Intermedics (1998).
7. G. J. Walters, 17th CARTS, Mar. 24-27, 1997.
8. B. Lavene, U.S. Pat. No. 5,614,111 (Mar. 25) (1997).
9. M. Mandel, ""You Ain't Seen Nothing Yet", Business Week, Aug. 31 (1998).

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