High energy density and high temperature multilayered polymer film capacitors

Deepak Langhe and Michael Ponting

PolymerPlus LLC, 7700 Hub Pkwy,
Valley View, OH 44125, dlanghe@polymerplus.net

ABSTRACT

Pulsed power DOD applications like railguns utilize metalized biaxially oriented polypropylene (BOPP) based capacitors for energy storage. Although, BOPP films offer extremely low loss, stable capacitance and long life at ambient temperature; the energy density in these films is limited to 2.4 J/cc at film level, which leads to large capacitor volume. Many other disadvantages include DC conduction losses at high temperature leading to capacitor failure. Increased energy density decreases the life expectancy exponentially. Increased energy density capability, high temperature stability while maintaining low losses is critical in pulsed power capacitors. PolymerPlus developed multilayered film technology demonstrated capacitors with higher energy storage capacity, low losses, while eliminating the high temperature limitations of present railgun capacitors. Using PolymerPlus coextrusion process, fabrication of high energy density films and first generation capacitor prototypes was demonstrated.

Keywords: high temperature capacitors, multilayered films, dielectrics, energy storage

1 INTRODUCTION

Capacitors are used in nearly all electronics and electrical applications such as computers, power electronics, hybrid vehicles, grid converters, and pulsed power. [1-3] Development of compact devices necessitated the size reduction of electronic components including capacitors. Development of compact capacitors while maintaining the desired energy storage capacity requires increased energy density capacity. Energy density of the insulating material is directly proportional to the dielectric constant and the square of the dielectric strength of the material. Therefore, high dielectric constant, high breakdown strength, and low losses are desired in a capacitor material to achieve high energy density.

Polymer film capacitors with graceful failure are more advantageous than ceramic and electrolytic capacitors for high-voltage/high current pulsed power, power conditioning applications. However, they also suffer from few disadvantages. Existing pulsed power applications utilize metalized, biaxially oriented polypropylene (BOPP) film capacitors due to their extremely low loss, stable capacitance, and long life at ambient temperature. However, the energy density of BOPP films is limited to approximately 2.4 J/cc in these applications and is accompanied by a significant DC conduction loss at 100 °C. It is known that continuous shooting (6-12 shots/min at 6.5-11 kV) tends to increase the capacitor temperature creating hot spots inside a railgun capacitor. Life expectancy of the BOPP capacitor is limited by the energy density. BOPP capacitors survive longer if operated at lower energy density. Also, thermal issues become significant in BOPP-based capacitors in railgun applications. For a commercial railgun capacitor, the life expectancy decreases exponentially as the required energy density increases. Meanwhile, the low energy density of BOPP films results in a large volume, as compared to the other types of capacitors. Therefore, it is highly desired to develop new dielectric films with higher energy density (at least twice that of BOPP), low loss (dissipation factor, tanδ < 0.01), and high operating temperature (> 125 °C) capabilities.

In another example, electric vehicles (EVs) and hybrid electric vehicles (HEVs) use DC-link capacitor, which supplies periodic high currents enabling quick energy transfer to the insulated gate bipolar transistor (IGBT) circuit and typically runs at higher temperature (> 100 °C). Although commercially available electrolytic capacitors offer higher energy density, they have short life at high temperature. Other capacitors such as ceramic and glass-based capacitors are still in research stage. Alternately, BOPP and polyethylene terephthalate (PET) based polymer film capacitor suffer from low energy density and limited high temperature performance for EV and HEV applications. Additionally, BOPP-based capacitors occupy more than 1/3rd of the total volume in power electronics components.

Polymer film capacitors are widely favored due to their high dielectric strength, low dielectric losses, high energy density and ease of film processing. Additionally, polymers are lightweight and inexpensive as compared to other capacitors. The most commonly used polymer films for capacitor applications are BOPP and PET. BOPP dielectric films have low loss (tan δ~0.0002) and low energy density (4.88 J/cm^3 at breakdown of 730 MV/m), while biaxially oriented PET film has a slightly higher energy density (6.0 J/cm^3 at breakdown of 600 MV/m) and moderate dielectric loss (tan δ~0.003). [2] Both BOPP and PET capacitor films show low energy density, unsatisfactory high temperature and high voltage performance. Both polymers exhibit excellent room temperature performance, however, significant deterioration of dielectric properties above 80 °C. Improving the high temperature and high voltage capability of polymer dielectric films can enable fabrication of compact and more efficient systems.

To overcome these challenges, the development of high energy density and high temperature capacitors, while maintaining the low losses, is desired for current and future applications. Multiple approaches combining high dielectric constant inorganic particles such as barium titanate, titanium dioxide with high breakdown strength polymers negatively impacted the breakdown properties. [4] Other approaches included development of new copolymers and modification of BOPP. These efforts had limited commercial viability and scale up challenges [5]

PolymerPlus has demonstrated, using licensed coextrusion technology, multilayering a high dielectric constant polymer (e.g., PVDF and its copolymers) and a high electric breakdown polymer (PC) results in the achievement of high breakdown strength, high discharged energy density, and relatively low loss. Combining poly(vinylidene fluoride) (PVDF) and its copolymers with a high breakdown strength linear polymer, such as polycarbonate (PC) or PET, into a layered structure using the multilayer film coextrusion technology led to the development of novel dielectric films with improved dielectric properties. [6-10] The PC/P(VDF-HFP) 70/30 32-layer film shows a high discharged energy density at breakdown (~13 J/cm^3), low dissipation factor (tanδ~0.005) and low hysteresis loss (<15% at 600 MV/m). Different from the ferroelectric P(VDF-*co*-hexafluoropropylene) [P(VDF-HFP)], which exhibits significant hysteresis in the D-E loop, the PC/P(VDF-HFP) 50/50 32-layer film showed a much higher energy density than that of the state-of-the-art BOPP, but a dramatically reduced hysteresis with linear D-E loops. It is known that PVDF and its copolymers are ferroelectric thereby causing significant hysteresis loss during dynamic poling processes. However, the ferroelectric hysteresis is completely suppressed in PC/P(VDF-HFP) multilayered films.

Since the T_g of the PC (145 °C) and the melting temperature (T_m) of PVDF-HFP (125 °C) in these films limits the high temperature use, newer material grades were investigated in this study. PolymerPlus has investigated multilayered film extrusion of PVDF homopolymer (melting temperature, T_m = 165 °C) with a high glass transition (T_g) polycarbonate (PC, T_g = 175 °C). Dielectric properties of 33 layered PC/PVDF films were investigated at room temperature (RT) and at 120 °C. The results provide insights into a unique opportunity to use multilayer coextrusion to meet the need for high energy density and higher operating temperature capacitors in many applications.

2 EXPERIMENTAL

PVDF homopolymer (Solef 6010 from Solvay), and high temperature PC (APEC 1745 from Bayer MaterialScience) were acquired and used for coextrusion trials. 33 layered films of PC/PVDF were fabricated using forced assembly layer multiplying melt coextrusion process as described previously.[10] PC was dried overnight at 80 °C under vacuum prior to the coextrusion processing. The film structure constituted alternating layers of PC and PVDF as shown in **Figure 1**. A sacrificial surface layer of LDPE was also added before the melt exited from the film die. The LDPE surface layers were used to achieve excellent surface finish and improved uniformity in the multilayered films (MLFs). The film thickness of 8 µm was ensured during the film processing. MLFs were tested for various dielectric properties including breakdown strength (BDS), energy density, and dielectric hysteresis. The film take-off unit was equipped with in-line removal of LDPE layers.

The breakdown strength (BDS) was measured with a Quadtech Guardian 20 kV HiPot tester using plane-plane electrodes and a voltage ramp of 500 V/s. The voltage was increased until breakdown occurred. Test samples were sandwiched between flexible electrodes consisting of metalized polypropylene films. The sample area was 2 cm^2 and controlled using a thick sample mask. Each measurement was repeated at least ten times.

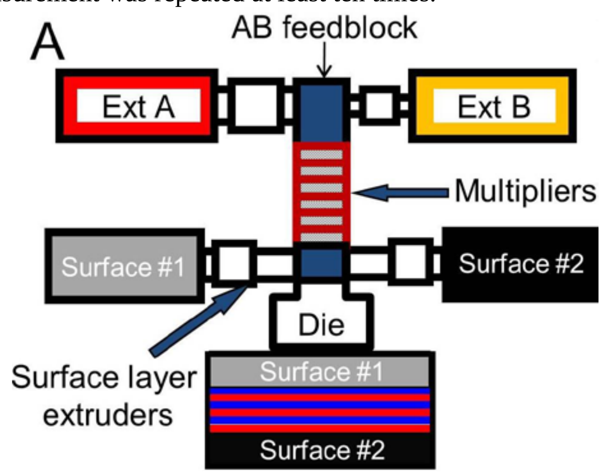

Figure 1: Multilayer coextrusion process at PolymerPlus

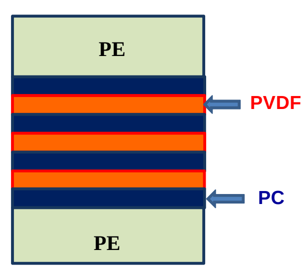

Figure 2: 33 layered PVDF/PC film structure with protective PE layers (removed in-line during processing)

The energy density of multilayered films was measured with a charge/discharge circuit. 1 cm gold electrodes were coated on both sides of the film samples using a sputter coater. A pulsed voltage with duration of 500 ms was

TechConnect Briefs 2015, TechConnect.org, ISBN 978-1-4987-4728-8

applied using a Quadtech Guardian 20 kV HiPot tester in increments of 0.5 kV. The electrodes and sample were immersed in mineral oil to minimize surface and corona discharge. The resulting charging and discharging currents were measured by placing two resistors (150MΩ and 100 kΩ) in parallel with the sample and recording the voltage across the precision 100 kΩ resistor with a data acquisition card (NI AT-MIO-16E-1). The energy density was determined by integrating the discharge current with respect to time.

Electric displacement−electric field (D−E) hysteresis measurements were carried out using a Premiere II ferroelectric tester from Radiant Technologies, Inc. The applied voltage was a bipolar triangular waveform at 1 Hz. Gold coated film samples with a 1 cm diameter were used for testing. For each sample, electric fields from 100 to 700 MV/m were applied to the sample in 50 MV/m increments.

All the measurements were carried out in a silicone oil (DPDM-400 Diphenyl Dimethyl Silicone Fluid) bath. High temperature measurements were performed at 120 °C in a heated oil bath.

The film rolls were metallized and wound into capacitors. Film capacitors in 1.1 to 6 μF range were fabricated using multilayer films. The capacitors were further tested for capacitance, dissipation factor, equivalent series resitance (ESR), and insulation resistance (IR). These properties were tested over 25 to 160 °C temperature range.

3 RESULTS

3.1 Multilayer Film Production

Continous coextrusion process was successfully used to fabricate multilayer film rolls up to 3000 ft length demonstrating process scalability. Typically 4-6 splices were required to fabricate these rolls. The multilayer films were then characterized for dielectric properties and then used for metallization and capacitor winding.

3.2 High temperature performance of PC/PVDF films

High temperature dielectric characterization of PC/PVDF films was carried out at 120 °C. The hysteresis increased with increasing PVDF content and poling electric field, which was attributed primarily to the enhanced DC conduction and increased ion migration in multilayered films. **Figure 3** shows the percentage energy loss as a function of electric field for different compositions at 120 °C. Below 300 MV/m, the hysteresis loop loss is below 20%, which is significantly lower than that for BOPP at 125 °C (i.e., over 50%). At 125 °C, ion migration loss is seen at 10-100 Hz and crystalline PVDF α_c loss is seen at 70 kHz A reasonably low tanδ of 1.5% is seen for the high T_g PC/PVDF 50/50 33-layer MLF at 1 kHz.

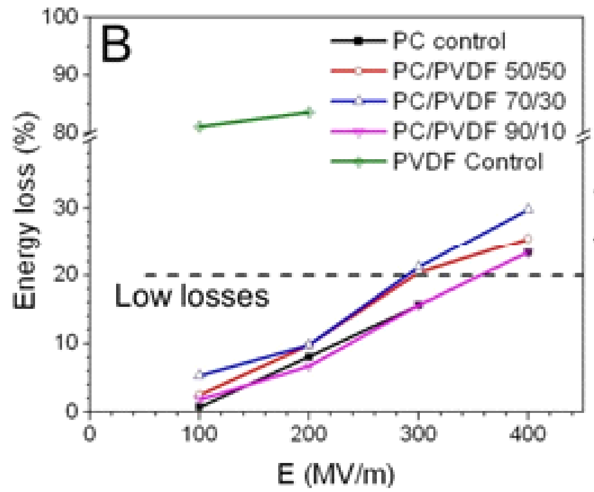

Figure 3: Energy loss as a function of electric field in PC/PVDF multilayer films

3.3 Capacitor Fabrication and Testing

PolymerPlus manufactured a first generation MLF capacitor prototype using high temperature PC/PVDF films. 2000 ft. film rolls are successfully metallized and slit using conventional techniques used for BOPP films (**Figure 4a**). The metallized films were further wound into capacitor prototypes. Two examples of capacitor prototypes – 1.4 and 3.2 μF – are shown in **Figure 4b**. The analysis of the capacitor was performed at 25-160 °C. Capacitance change and dissipation factor change over this temperature range are shown in **Figures 5a** and **5b**. The multilayer film capacitors show a very stable capacitance at 25-160 °C. The measured capacitance change is less than 0.1% between 25 and 160 °C. The DF (tanδ) is 0.6% at room temperature, which increases to 1% at 80 °C and further decreases to 0.8% at 140 °C. In addition, the breakdown voltage properties of the capacitors also show improvements over comparable BOPP and PET film capacitors. The properties are compared with BOPP and PET film capacitors in **Table 1**.

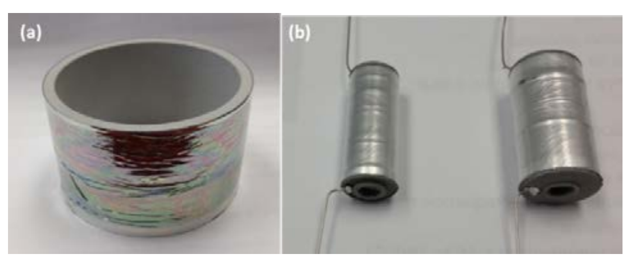

Figure 4: (a) 38.1 mm metallized MLF film roll produced by slitting 9” wide x 2000 ft long film, (b) examples of two prototoypes – 1.4 μF and 3.2 μF

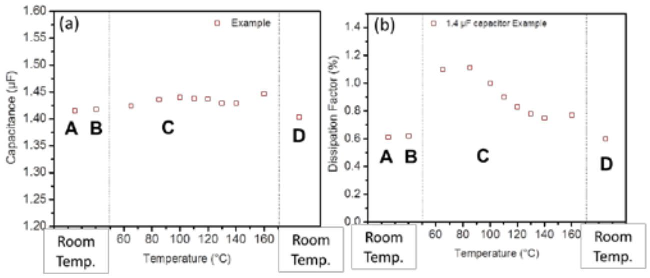

Figure 5: (a) capacitance change over 25 to 160 °C temperature range, (b) dissipation factor change over 25 to 160 °C temperature range. [A= tested after drying for 12 h at 40 °C, B= tested after clearing at 100- VDC for 2 min, C= 25 to 160 degree temperature range, D = tested after temperature sweep]

Capacitor Prototype	Dissipation Factor (%)	Capacitance change	Breakdown strength (MV/m)
Multilayer Films	0.6%	< 0.1 % (25-160 °C)	200-350
BOPP	0.02- 0.1%	3 % (25 -100 °C)	200
PET	0.5%	10-15% (-25-125 °C)	170
PPS	<1%	< 2 % (25 -125 °C)	--

Table 1: Comparison of multilayer film capacitor with commerical BOPP and PET capacitors

3.4 Conclusions

Multilayered film based capacitors have demonstrated signficantly improved dielectric properties and improved high tempearature performances. Significantly improved energy desity as compared to BOPP and PET, with reasonably low losses. The first generation capacitor prototype demonstrated less than 1% change in the capacitance over a wide temeprature range of 25 to 160 °C, which was significantly better than many commercial capacitors. The improved properties allow use of multilayer film capacitors in many applications including railguns and power electronics in electric vehicles or hybrid electric vehicles.

REFERENCES

[1] W.J. Sarjeant, J. Zirnheld, F.W. MacDougall, IEEE Transactions on Plasma Sciences, 26, 1368 (1998)

[2] I. Husain, Electric and Hybrid Vehicles: Design Fundamentals, CRC Press: Boca Raton, FL, (2010)

[3] R. Teodorescu, M. Liserre, P. Rodriguez, Grid Converters for Photovoltaic and Wind Power Systems, Wiley: Chichester, U.K., (2011)

[4] J. Wang, F. Guan, Q. Wang, J. Huang, W. Li, L. Zhu, PMSE Preprints, 100, 437 (2009)

[5] B. Chu, X. Zhou, K. Ren, B. Neese, M.R. Lin, Q. Wang, F. Bauer, Q. M. Zhang, Science, 313, 334 (2006)

[6] M. Mackey, A. Hiltner, E. Baer, L. Flandin, M.A. Wolak, J. S. Shirk, Journal of Physics D: Applied Physics, 42, 175304 (2009)

[7] M.A. Wolak, A.S. Wan, J.S. Shirk, M. Makey, A. Hiltner, E. Baer, Journal of Applied Polymer Science, 123, 2548 (2012)

[8] M. Mackey, D.E. Schuele, L. Zhu, L. Fandin, M.A. Wolak, J.S. Shirk, A. Hiltner, E. Baer, Macromolecules, 45, 1954 (2012)

[9] Z. Zhou, M. Mackey, J. Carr, L. Zhu, L. Flandin, E. Baer, Journal of Polymer Science Polymer Physics, 50, 993 (2012)

[10] M. A. Wolak, M-J Pan, A. Wan, J.S. Shirk, M. Mackey, A. Hiltner, E. Baer, L. Flandin, Applied Physics Letters, 92, 113301 (2008)