Nanocomposite Film Dielectrics for High Temperature Power Conditioning Capacitors

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Abstract

Emerging power electronics in a broad range of military, aerospace, hybrid vehicle, renewable energy and drilling applications rely on advances in dielectric materials for capacitors. Compact capacitors possessing low dielectric loss and high operating temperature capability are needed for power conditioning in advanced converter and inverter designs for these applications. Wound film capacitors represent the preferred capacitor technology but are limited by low operating temperature capabilities, < 150°C, and low volumetric efficiency, capacitance per unit volume less than 1.0 µF/cc.

TPL is developing processes and manufacturing techniques for fabrication of advanced capacitor films comprised of high temperature polymers modified with ceramic nanoparticles. The selected polymers enable high temperature operation and the ceramic nanoparticles enhance volumetric efficiency by increasing the dielectric constant. The fabricated films are adaptable to conventional wound film capacitor construction methodologies.

This paper provides an overview of TPL's experience to-date with a film dielectric material system comprised of fluorenone polyester polymer and titanate nanoparticle filler. The fluorenone polyester polymer was selected to provide a stable operating temperature of at least 200°C, while the addition of the titanate powder increases the dielectric constant and, in turn, the volumetric efficiency of wound film capacitors constructed with this film system. Status and ongoing capacitor development issues are provided relative to the intended high temperature power conditioning applications.

Key Words: fluorenone polyester, nanocomposite, capacitor, volumetric efficiency

General Issues Surrounding High Temperature Capacitor Films

Various high temperature polymers are available today such as polyimide, silicone, polyethersulfone and polytetrafluoroethylene but have not been manufactured into capacitor film required to achieve high volumetric efficiency. (Limitations on process-ability for capacitor film are unique to each polymer and are beyond the scope of this paper.) One exception is fluorenone polyester (FPE), a polymer originally developed by 3M in the 1980s. FPE provides the physical properties, process-ability and thermal properties required for the fabrication of capacitors capable of operating at temperatures in excess of 200°C. Work funded by the US Department of Energy supports progress toward this development of FPE capacitors [1].

While capacitors with increased operating temperature capability appear attainable, achieving increased volumetric efficiency is uncertain with current polymer technology. Limits to the parameters controlling volumetric efficiency, as described below, are largely defined.

$$\text{Volumetric Efficiency} \propto [\varepsilon/t] \times PF$$

where: ε = dielectric constant
t = capacitor film thickness
PF = capacitor packaging factor (active/total volume)

The dielectric constant of all low dielectric loss polymers falls within a narrow range, 2.5 to 3.5. Capability for producing and processing capacitor film is limited to a narrow thickness range, 2.0 µm to 5.0 µm. Packaging efficiency of dielectrics in wound film capacitors typically falls within a narrow range, 0.65 to 0.75.

TPL's approach to producing high temperature capacitors with high volumetric efficiency involves modifying polymers to achieve an increased dielectric constant. Thermally stable ceramic dielectric fillers possessing a high dielectric constant (k > 1,000) are uniformly dispersed in the polymer to form a composite (Figure 1). Incorporation of sub-micron titanate particles have been used to increase the polymer dielectric constant by a factor 20, e.g., 3.0 to 60. In the case of capacitor film, a filler concentration is used that does not significantly impact the mechanical properties, dielectric loss or voltage stress capability. Thin capacitor films, 2.0 µm to 5.0 µm, can be produced with several times greater dielectric constant, relative to the unmodified polymer. This increase in dielectric constant is directly proportion to increased volumetric efficiency.

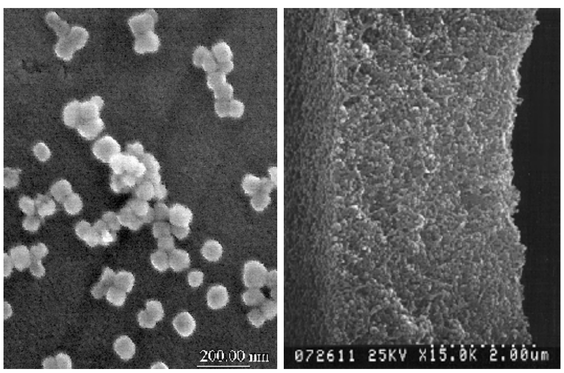


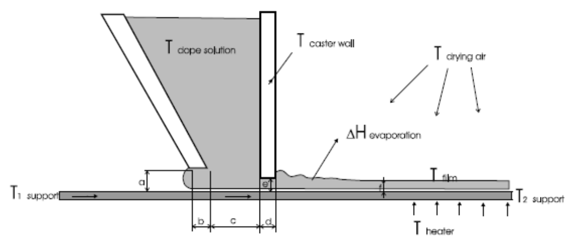
Figure 1: Micrograph of TPL titanate particles (50 nm) and composite dielectric film (4 µm).

Processing of the dielectric film into highly efficient and reliable capacitor designs is achieved in wound configurations that provide tolerance to shorting due to dielectric failure at voltage. Self-healing, or soft breakdown, behavior represents a major reliability advantage that metallized-film capacitors possess. It derives from the thin metal layer (measured in angstroms) of metal that is applied to the film to form the capacitor plates. When a dielectric breakdown occurs, electrical charge flows rapidly to the breakdown site. This large surge of current vaporizes the metal around the breakdown site. Removal of the metal around the breakdown site isolates the breakdown site from the voltage stress and, thus, the capacitor self-heals. In contrast, typical ceramic capacitors have relatively thick electrodes that are printed from metal particle dispersions and co-fired with the ceramic; accordingly, there is no self-healing behavior.

Through a combination of ceramic processing and solvent-based coating processes, TPL has engineered composite dielectric films that possess the electrical and physical properties required for producing capacitors with a substantial increase in operating temperature and volumetric efficiency. TPL has investigated capability for producing composite capacitor films of several high temperature polymers including polyimide, silicones, epoxies, polyetherimide, polysulfone, polyethersulfone and fluorenone polyester. FPE nanocomposite has been pursued to the largest extent to-date and is, therefore, selected for this description of development and fabrication aspects. FPE itself provides a stable operating temperature in excess of 200°C. As described in this paper, titanate nanoparticle modifications to FPE can provide a factor of two to three increase in capacitor volumetric efficiency and operating temperature capability of at least 200°C.

Film Fabrication Methodology

The film fabrication methodology utilized by TPL involves casting of the nanoparticle-polymer dispersion onto a supporting and releasable substrate using a doctor blade casting head (Figure 2), and in-line ovens to remove solvents from the cast solution (Figure 3). The result is nanocomposite film on a releasable substrate.

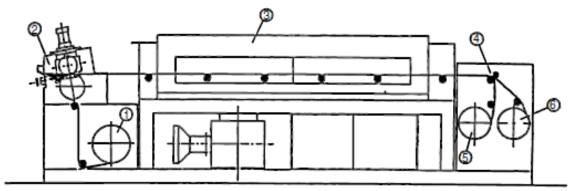


a. – f. coating head dimensions
T temperatures
H enthalpy of solvent(s)

Figure 2: Doctor blade casting head [2]

TPL has investigated several techniques for fabrication of capacitor-grade nanocomposite films in the thickness range of 2 µm to 15 µm. Given the ability to solvate the polymer resin in the nanocomposite system, film fabrication by doctor blade coating on an ultra-smooth substrate has been found to provide the best and most consistent results. Other techniques investigated include slot die, rod and gravure coating; however, each of these alternate techniques was found to have at least one aspect that precluded quality film formation with acceptable thickness uniformity in a production process.

Separation of the film from the substrate can be accomplished as a part of the in-line casting and drying operation, as depicted by the support film and product film winders (Figure 3). Alternatively, TPL has developed methods for separation of the film and substrate during the capacitor winding operations. Separation at winding enables especially delicate films to be conveyed through intermediate operations such as metallization, slitting and spooling with reduced susceptibility to film damage.



1 = support film un-winder
2 = casting head (doctor blade)
3 = flat bed dryer
4 = separation point
5 = support film winder
6 = product film winder

Figure 3: Cross-section of film casting line [2]

Film and Capacitor Processing

Conditions and processes have been defined for fabricating quality FPE nanocomposite film with a thickness deviation less than 5%. TPL's film fabrication line has three independent oven zones, a nominal line rate of 90 meters per hour and a coating width of 375 mm and is housed in a Class 100 clean room (Figures 4 and 5). Film thickness and uniformity are controlled rheologically through solvent selection, polymer solution viscosity and polymer concentration in solution, and physically through film feed rate and die head adjustments. Time and temperature profiles, and exhaust rates play a major role in the drying rate as the film is conveyed through the oven zones.

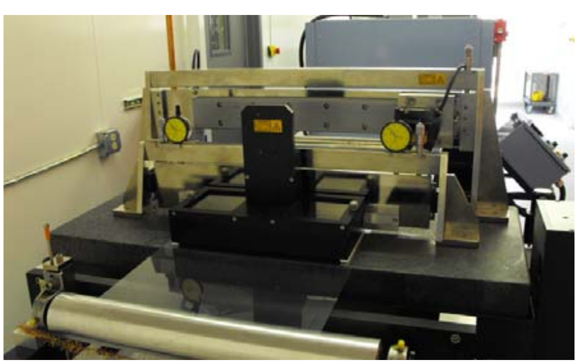


Figure 4: Film fabrication line, coating head area

At least 100 m^2 of continuous quality film is required for the film processes necessary to support prototype capacitor fabrication. This line provides such capability as well as a clean environment to minimize particulate inclusions that can significantly degrade the film's voltage reliability. All major film fabrication work on the FPE nanocomposite has been successfully transitioned to this pilot-scale line.

Figure 5: Film fabrication line, oven exit area

A significant number of film production trials focused on optimizing coating parameters have led to film quality that supports consistent capacitor performance. Film properties are detailed in previously reported data [3]. To-date, all process parameters required for fabricating FPE nanocomposite capacitors have been successfully addressed. Critical process stages required to convert the FPE from the nanoparticle dispersion to the final capacitor section have been established (Figure 6). Film rolls of the FPE composite were metallized, slit and spooled into roll pairs suitable for capacitor winding. Provided metallized film in roll stock, capacitor sections were wound, terminated and packaged. Packing included a polyimide wrap with ends filled with a high temperature epoxy (Figure 7).

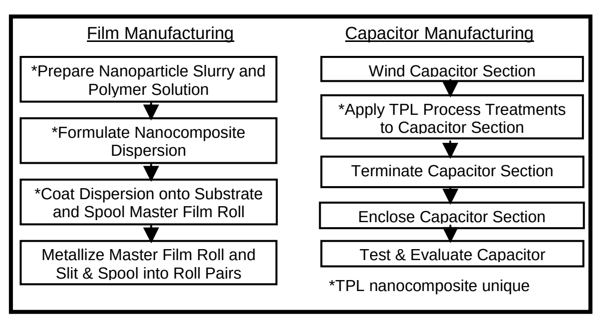


Figure 6: Process stages for FPE nanocomposite capacitor fabrication

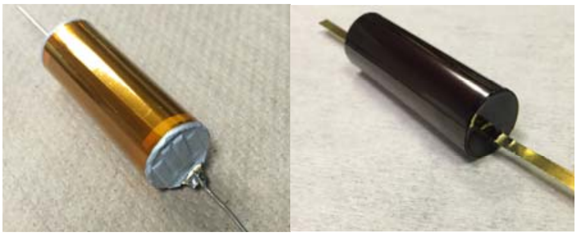


Figure 7: Capacitor winding with end connection (left) and wrap and fill encapsulation (right)

Recent Development Focus for Capacitor Life at 200 °C

Ongoing development activities are focused on addressing performance issues relative to capacitor life. Prototype capacitors (10 to 20 μF) are being routinely fabricated with FPE nanocomposite film, nominal thickness of 4.0 μm. Testing of these capacitors supports a largely independent temperature and frequency behavior with less than ± 5% change in capacitance from -55 to +200 °C and 100 Hz to 100 kHz. Most recent activities have shifted to resolving capacitor degradation issues identified in extending capacitor test and evaluation from less than 5 hours to greater than 100 hours. A systematic development approach was required to deconvolute the impact of the dependent capacitor stresses. Limitations for capacitor life relative to temperature, DC voltage and ripple current were identified and addressed in a sequential manner. Three critical issues identified relative to capacitor life included;

1. Loss in capacitor end connection integrity,
2. Increase in film metallization resistivity, and
3. Capacitor failure due to electrical shorting.

Loss in capacitor end connection integrity was observed in extended capacitor life testing. Zinc flame sprayed end connections on capacitor windings degraded during ripple current operation at 200 °C. Capacitor series resistance progressively increased and ultimately resulted in loss of electrical connection to the metallized film. The issue was originally assumed to be a result of high ripple current since the rate of degradation was found to be proportional to the magnitude of ripple current.

A series of experiments revealed metal oxidation between the zinc end spray and aluminum film metallization to be the source of end connection degradation. The product of the oxidization appears as a powder residue between the between the zinc and aluminum. While high ripple current accelerated this behavior, likely due to increased temperature from localized heating, oxidation was found to occur without DC voltage bias and ripple current.

Oxidation of the end connection at high temperature was found to be enabled by the presence of moisture and oxygen. Confirmation of this behavior was validated by vacuum drying capacitor sections and performing extended holds in dry nitrogen at temperatures in excess of 200 °C. No loss in end connection integrity or increase in ESR was apparent.

Modified processing procedures and capacitor encapsulation were successfully introduced to eliminate oxidation of end connections. All film and capacitor windings are stored in dry nitrogen. Capacitors are vacuum dried at temperature following atmosphere exposure and prior to encapsulation. Previous capacitor packaging with a silicone encapsulant was replaced with a polyimide wrap and high temperature epoxy end fill (Figure 7). Despite being hydrophobic, silicones exhibit moisture and gas permeability several orders of magnitude greater than most polymers [4].

Provided stable end connections, capacitor life testing at temperature resumed but quickly led to identification of the second critical issue; increase in metallization resistivity. Capacitors tested over the course of several days at 200 °C exhibited a progressive increase in ESR. Further, the rate of increase in ESR was found to be proportional to the DC voltage bias. Extended tests revealed the increase in ESR led to a loss in measured capacitance. Failure analysis of these capacitors and evaluation of the film revealed areas of high metallization resistivity. Continuity of the metallization was lost in select areas, consistent with the observed capacitance loss.

Additional capacitor evaluations and a thorough literature review revealed the increase in metallization resistivity is associated with electrochemical metal corrosion [5-7]. The relatively thin vapor deposited aluminum (< 100 nm) is very susceptible to metal oxidation which results in increased resistivity. Key factors influencing the oxidation rate and increase in surface resistivity include temperature, voltage and leakage current.

In the interest of operating at or above 200 °C, capacitor evaluations were directed at identifying the role of voltage stress and leakage current on the oxidation behavior. A test configuration was established to monitor leakage current through the capacitor during voltage testing at temperature (Figure 8). The capacitor (DUT) was placed under voltage in a temperature controlled convection oven and the leakage current was monitored using a current viewing resistor (R2). A second resistor (R1) was placed in series with R2 to prevent over voltage to the analog to digital converter (Dataq DI-149). Output from the Dataq DI-149 allowed for monitoring of leakage current and temperature as a function of time. Leakage current data from the capacitor testing was normalized with respect to voltage and capacitance by calculating the product of insulation resistance and capacitance, i.e., insulation resistance normalized for capacitance, MΩ-µF .

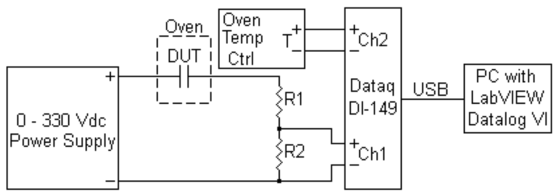


Figure 8: Capacitor insulation resistance test configuration

The increase in ESR and loss in capacitance due to metal oxidation was found to depend significantly on the capacitor insulation resistance. Capacitor performance was found to be stable when operating with an insulation resistance above 10 MΩ-µF and demonstrate progressively higher degradation rates below 10 MΩ-µF. Obtaining a leakage current consistent with an insulation resistance greater than 10 MΩ-µF was achieved by reducing the temperature or reducing the voltage stress. At the target operating voltage of 300 V, it was determined that the operating temperature for an insulation resistance greater than 10 MΩ-µF was less than 150 °C. This threshold insulation resistance corresponds to a leakage current of approximately 0.5 mA for a 15 µF capacitor operating at 300 V.

Provided an operating limit of 150 °C due to excessive leakage current, the insulation resistance of the FPE nanocomposite film became a primary focus. Material preparation and film treatments beyond the scope of this paper were investigated in support of increased capacitor insulation resistance above 150 °C. Material purification and thermal treatments were directed at eliminating ionic and polymeric charge carriers that contributed to leakage current at voltage and temperature. While progress continues in this area, most recent results from the FPE nanocomposite material and process refinements support a significant increase in capacitor insulation resistance over the full temperature range (Figure 9). Leakage current was reduced at the target operating voltage to a level necessary for extended operational life at 200 °C. Electrochemical aluminum corrosion which results in increased metallization resistivity is minimized.

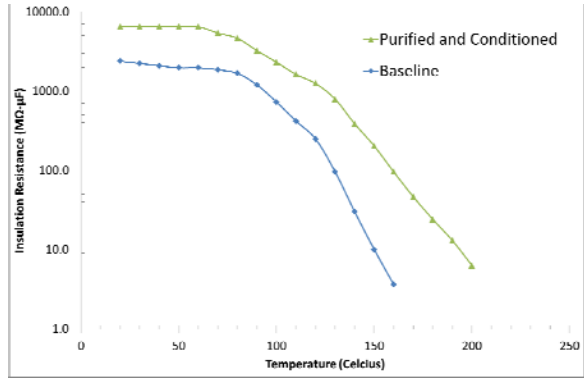


Figure 9: Insulation resistance versus temperature before and after FPE nanocomposite purification and conditioning steps

A final capacitor life issue currently being addressed is voltage reliability. Select capacitors have demonstrated predictable and stable performance for several hours followed by an event that results in increased leakage current and often electrical shorting. Characterization of these capacitors supports localized film failures that extend through several layers of the capacitor winding. Normal clearing or self-healing behavior which is characteristic of metallized film capacitors does not occur. Incomplete metal clearing around the defect site and/or carbon residue from the clearing event supports charge transfer, i.e. leakage current. This charge transfer results in localized resistive heating that can cause progressive damage to adjacent film layers and result in a runaway event that leads to electrical shorting of the capacitor.

Capacitor conditioning processes are being modified in effort to eliminate film defect sites that result in progressive capacitor damage. The rate and magnitude of voltage applied to capacitors at room temperature has been found to have a significant impact on the clearing behavior. Pulse charging to a voltage higher than operational has provided improved clearing efficiency and capacitor reliability. The relatively short high voltage pulse (< 1.0 msec) allows for clearing of metallization around the film defect site with minimal damage to the capacitor. Applying a voltage greater than the operation voltage increases the distance metallization is removed around the defect site, therefore reducing charge transfer through the defect site. Continued optimization of this voltage conditioning protocol supports improved reliability under life testing.

Provided resolution of these three critical capacitor life issues, future capacitor testing will include ripple current. Capacitors which demonstrate stable capacitance, ESR and IR at voltage and temperature will be tested with ripple current, switching frequencies between 5 kHz and 150 kHz.

The basic ripple test configuration is a constant-charge, pulse discharge arrangement (Figure 10). DUT denotes the capacitor being tested. Cooling and heating apparatus have been adapted to the test configuration to allow adjustment of the DUT temperature from -55 to +300 °C. Oscilloscope images of the voltage and current waveforms are acquired during ripple testing (Figure 11).

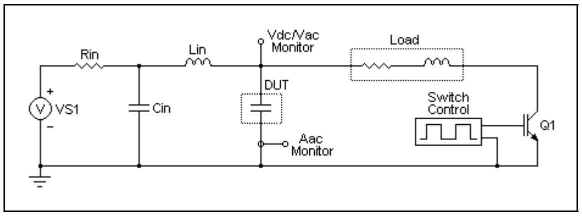


Figure 10: Capacitor ripple current test configuration

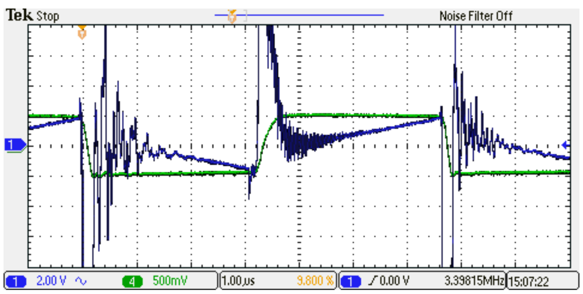


Figure 11: Ripple test voltage and current waveforms (AC voltage on Ch1, current on Ch4 @ 0.1V/A)

Conclusions

TPL's work with FPE nanocomposite film to-date has demonstrated the potential for achieving compact, high temperature filter capacitors for emerging power conditioning applications.

The principle advancement over high temperature polymer films is an increase in dielectric constant by a factor of two through the addition of titanate nanoparticle fillers. The volumetric efficiency of the FPE nanocomposite film capacitors is projected to be greater than 1.0 μF/cm^3 for high ripple current operation at 300 V_{dc}.

Most recent development activities have focused on addressing technical issues that have limited capacitor life at 200 °C. Oxidation of capacitor end connections was eliminated with proper capacitor packaging. Degradation of film metallization was addressed through material and process refinements to increase capacitor insulation resistance. Continued focus is being directed at improving capacitor reliability through capacitor voltage conditioning.

Overall, significant progress has been made toward producing compact FPE nanocomposite capacitors for power conditioning operation at 200 °C in advanced converter and inverter designs.

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