E. High-Temperature Film Capacitors

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Contractor: Sandia National Laboratories, Albuquerque, New Mexico
Prime Contract No.: 04-94AL85000

Objectives

- Develop a replacement technology for aluminum electrolytic dc bus capacitors currently used for fuel cell/electric hybrid vehicles.
- Develop a high-temperature polymer dielectric film technology that has dielectric properties technically superior to those of aluminum electrolytic dc bus capacitors and that is of comparable or smaller size.
- Scale up cost-competitive polymer film dielectric technology.
- Develop high-volume production process for dielectric film roll fabrication.
- Fabricate prototype capacitors.

Approach

- Contact automobile design and component engineers, dielectric powder and polymer film suppliers, and capacitor manufacturers to determine state-of-the-art capabilities and to define market-enabling technical goals.
- Develop a project plan with automobile manufacturers and large and small capacitor companies to fabricate polymer dielectric sheets suitable for FreedomCAR capacitor manufacturing.
- Synthesize unique conjugated polyaromatic chemical solution precursors that result in dielectric films with low dissipation factors (DFs) and excellent high-temperature dielectric properties.
- Develop polymer film processes and technologies that will lower costs to permit competitive high-volume capacitor manufacturing.
- Interact with Oak Ridge National Laboratory (ORNL) with regard to mechanical characterization of films.

Accomplishments

- Invented chemical synthesis procedures that resulted in polymer films with four times the energy density of commercial polyphenylene sulfide (PPS) at 110°C. Scaled-up hydroxylated polystyrene (PVOH) films exhibited dielectric constants of 4.7 and DFs of 0.009 at temperatures of up to 110EC, thus meeting technical requirements for commercialization.
- Collaborated with TPL, Inc., and Steiner Corporation to adjust high-volume metallization procedures for Sandia National Laboratories (SNL) 10-in.-wide, 450-ft-long dielectric film.
- Initiated a project to investigate the effects of three different cross-linker species and their concentrations on the dielectric and mechanical properties of SNL PVOH films. This effort would permit fabrication of wound capacitors by high-volume metallization processing.
- Collaborated with ORNL to characterize mechanical properties of PVOH films.

Future Direction

- Perform extensive electric field and temperature characterization to determine that SNL polyfilm dielectrics will meet FreedomCAR requirements for breakdown field and DF for temperatures from –40 to 110°C.
- Fabricate and characterize 1-µF wound capacitors using non-high-volume metallization techniques to determine if they will meet General Motors (GM) requirements. Supply capacitors to GM, Ford, and Chrysler for testing in inverter-type environments.
- Have large-value (20- to 200-µF) capacitors fabricated by vendor(s) evaluated by GM and SNL in simulated electric hybrid vehicle environments.
- Develop chemical synthesis procedures for high-performance, more cost-effective films.

Results

Strategy and Interactions

SNL has actively interacted with a number of representatives from the automobile industry to obtain their perspective on what is needed for 2004 automobiles. In FY 2003, SNL continued its emphasis on the development of polymer film dielectrics for two reasons. First, GM has been adamant about soft breakdown dielectric film technology—a phenomenon that bulk ceramic capacitors do not exhibit. Second, emphasis on polymer dielectrics provides greater balance of the DOE effort between polyfilm and ceramic technologies, as requested by the Electrical and Electronics Tech Team. SNL has developed a close working relationship with the Advanced Technology Vehicles Division of GM. Based on phone calls and e-mail exchanges with GM staff that outlined technical progress and component qualification procedures, SNL has modified project plans for the development of polymer film dielectrics for FreedomCAR applications.

These interactions led us to the conclusion that the most viable replacement technology for electrolytic dc bus capacitors by 2004 is multilayer polymer film capacitors. Reducing the size of the polymer capacitors was most often cited by automobile design engineers and capacitor manufacturers as a needed technology-enabling breakthrough. In addition, it is necessary to improve high-temperature (110EC) performance while keeping the technology cost-competitive. For polymer film dielectrics, based on the GM 2004 criteria for capacitance density of 2.0 $\mu F/cm^3$, the team agreed that if a polyfilm of K = 4.5 could be developed that met the operating temperature requirements, then that film would be suitable for scale-up.

Based on the criteria from GM, an individual dielectric layer thickness of approximately 3 µm for polyfilm capacitors is projected. These thickness values are based on operating field strengths of 2 MV/cm for the newly developed polyfilm capacitors. Based on these assumptions and on measurement of presently available commercial capacitors, size comparisons and capacitance densities were obtained for 500 µF dc bus capacitors for different technologies. Soft breakdown behavior and lower cost are assets for polymer film

capacitors. The projected polymer film capacitor volume was calculated assuming that there is 40% non-active capacitor space and 200-nm thick electrodes are used. Note that the volumetric capacitance efficiency for a K = 4.5 polyfilm capacitor of 2.4 $\mu F/cm^3$ exceeds the near-term commercialization goal of 2 $\mu F/cm^3$.

Polymer Film Dielectric Development

SNL polymer film dielectric development has been based on the request from manufacturers that the new polyfilm dielectrics have voltage and temperature stability equivalent to that of present PPS technology. Thus a structural family of polymer dielectrics has been designed and synthesized to meet two of the most stringent FreedomCAR requirements: (1) low dielectric loss and (2) extremely good temperature stability. A patent disclosure has been initiated covering the design and synthesis techniques for this polymeric family. A further criterion for wound capacitors is that PVOH films can be adequately released from underlying carriers without tearing. In FY 20O3, we investigated three different cross-linker species at four different concentration levels in an attempt to enhance the ductility of our PVOH-based polymer. Our baseline cross-linker species was VEctomer 4010 at the 30 wt% level. Figure 1 shows schematic diagrams of the three different types of cross-linkers evaluated, VEctomer 4010 and 5015 and tetraethylene glycol divinyl ether (TEGDE). Structurally, these cross-linkers varied in the amount of rigid benzene cores and the density of vinyl ether termini.

PVOH films were synthesized using MEK solvent—similar to that used for casting at Brady Corporation of Milwaukee. Concentrations of 5, 15, 20, and 30 wt% were investigated. It is encouraging that we were able to synthesize films that had reasonable dielectric loss at low cross-link addition levels. Based on the work of Wereszczak, films with less than 30 wt% cross-linker have slightly lower hardness and elastic modulus. An example of low dielectric loss (low DF) with low cross-link density is shown in Figure 2 for VEctomer 5015 cross-linker. The dielectric constant and DF were measured at 1 kHz and 25°C in Figure 2. DFs of 0.005 were measured for the 5 wt% cross-linker addition at 110°C as well as for the 25°C measurements shown. Breakdown strengths appeared quite reasonable, in the 2.2 to 4.2 MV/cm range, for these spin-deposited films of approximately 0.5 µm in thickness on aluminum-coated silicon wafers. These measurements were made

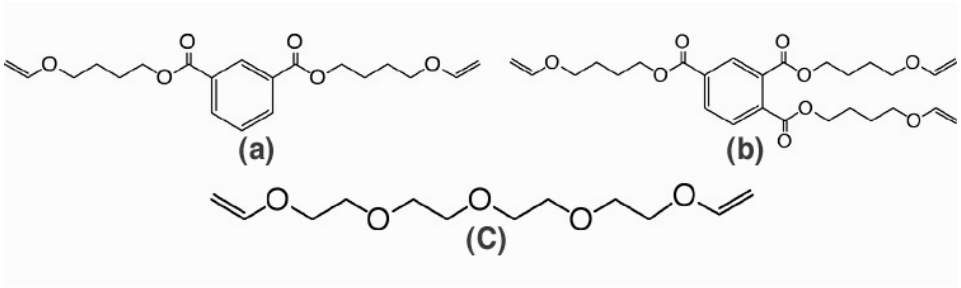


Figure 1. Schematic diagrams of three different cross-linkers: (a) VEctomer 4010, (b) VEctomer 5015, and (c) TEGDE

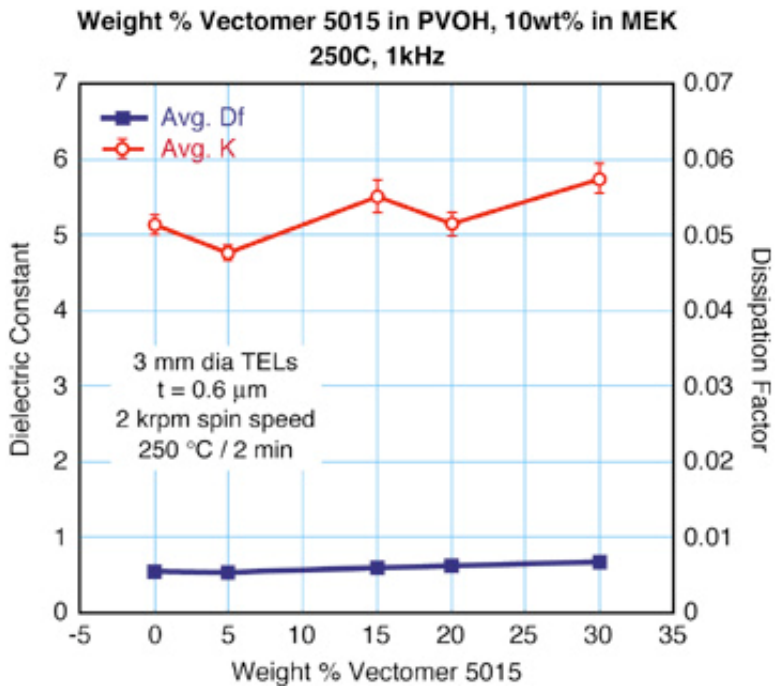


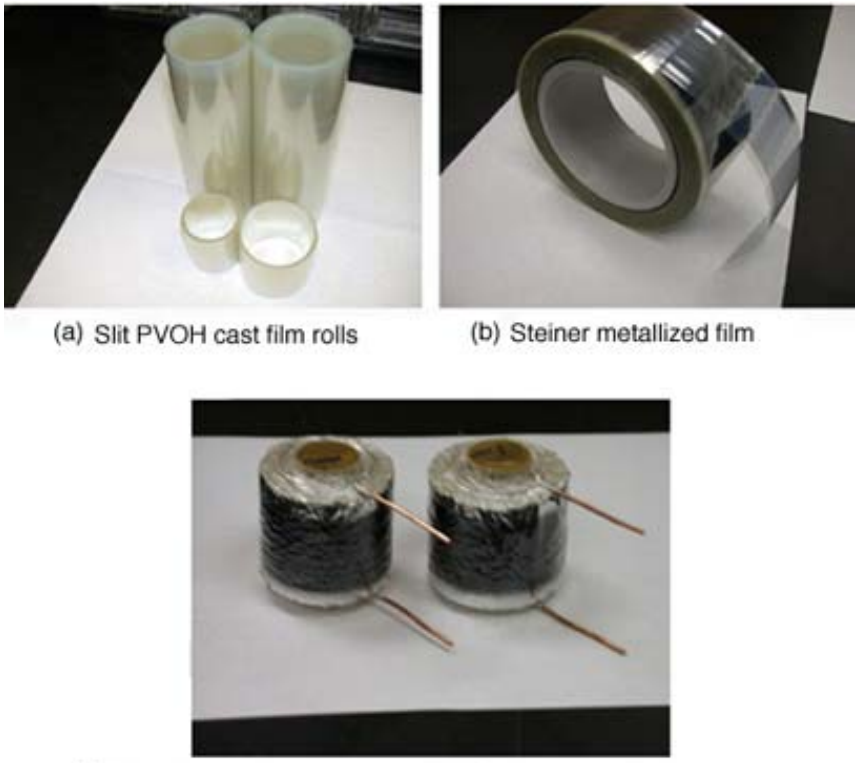
Figure 2. Dielectric constant and dissipation factor of SNL hydroxylated polystyrene film as a function of VEctomer 5015 cross-linker concentration.

using 3-mm-diam gold electrodes. Based on mechanical property data, we will select one of the lower (less than 30 wt%) cross-link concentration films for scale-up at Brady Corporation.

Figure 3 is a pictorial view of our PVOH film scale-up activities in FY 2003. Continuous slot-die-cast PVOH polymer film sheet is shown in Figure 3(a). The PVOH film sheets deposited on mylar carriers range from 20 to 50 ft in length. The 10-in.-wide film roll is then slit to 2-in. width for capacitor winding. We worked with TPL of Albuquerque to fabricate these slit rolls. Development of technology that was more amenable to high-volume production required interaction with Brady Corporation. We were able to cast 450-ft lengths of 10-in.-wide polymer film using the Brady prototype caster on 6-in.-diam mandrills. A high-volume electrode deposition process step is essential to manufacturing large-value capacitors with good volumetric efficiency. Steiner Corporation deposited aluminum electrodes on SNL films by a proprietary high-volume manufacturing process. The slit film roll electroded by Steiner is shown in Figure 3b. Because our polymer film tore during winding, the cure temperature of the PVOH film was decreased and the Steiner process was modified. Two wound polymer film capacitors of the modified process are shown in Figure 3c. Silver epoxy terminations were used after the zinc flame spray termination process was unsuccessful. Our dielectric film thickness is presently 4 to 5 µm for these capacitors.

Summary

Critical economic and technical issues for improvement of dc bus capacitors for FreedomCAR vehicles were determined through discussions and visitations with automobile design engineers, chemical synthesis companies, and capacitor manufacturers. PVOH film dielectric development was emphasized in FY 2003, and we have developed a multi-step project



(a) Slit PVOH cast film rolls (b) Steiner metallized film

(c) Wound capacitors using modified Steiner metallization process

Figure 3. SNL PVOH film scale-up activities.

plan for large-scale commercialization of polymer film dc bus capacitors. In FY 2003, we developed, in conjunction with TPL, a continuous process for fabricating 450-ft-long rolls of SNL PVOH sheets. We investigated several different aspects of capacitor fabrication, including lower-temperature cures and adjustment of deposition parameters at Steiner Corporation to minimize the brittleness of SNL PVOH films. There are different termination procedures for wound polymer film capacitors. SNL polymer film wound capacitors of 1-µF capacitance were fabricated using two different termination techniques, metallized paper and high-volume electrodes, and with and without oil backfilling. These capacitors met the extended temperature requirements for fuel cell vehicles. In addition, we are supplying—on a continuous basis—dielectric films to Andrew Wereszczak of ORNL from our scale-up and development activities. Understanding mechanical property–process

relationships is critical to developing film technology that exhibits adequate release from the underlying carrier. In FY 2004, we will concentrate our efforts on fabricating capacitors using aluminum foil rather than high-volume metallization processing. SNL PVOH film rolls fabricated at Brady Corporation will be used to fabricate a series of 1-µF and larger capacitors for evaluation by SNL, ORNL, GM, Ford, and Daimler Chrysler.

Presentations and Publications

1. D. Wheeler and G. Jamison, "Novel Polymer Film Synthesis Routes of Voltage and Temperature Stable Dielectrics," October 5, 1999.

2. B. A. Tuttle, D. Wheeler, G. Jamison and D. Dimos, "dc Buss Capacitors for PNGV Power Electronics," *Automotive Propulsion Materials 2002 Annual Progress Report*, U.S. Department of Energy, pp. 27–32, October, 2002.

3. B. Tuttle, J. Wheeler, G. Jamison, D. Williams, D. Wheeler, J. Cesarano and P. G. Clem, "Dielectric Materials for Fuel Cell Vehicles and Pulsed Discharge Applications," presented at the Dielectric Materials and Components for Pulsed Power Applications Workshop, Arlington, Virginia, June 2–3, 2003 (invited), to be published in the proceedings.