2015 DEIS Graduate Fellowship Proposal

Study of High Field and High Temperature Conduction Losses in Strongly Dipolar Polymers

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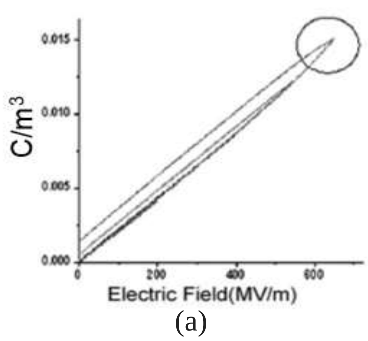
Introduction

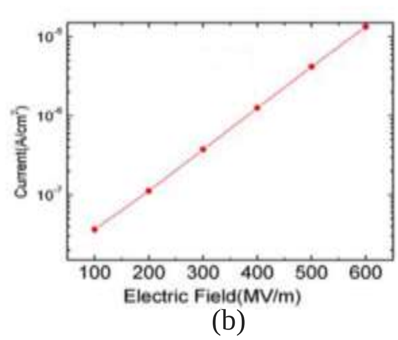
The development of efficient, high-performance materials for electrical energy storage is essential to meet the ever-increasing demands for electrical energy. Dielectric materials with high energy density are desirable for a broad range of modern power electronic systems such as medical devices, hybrid electrical vehicles (HEVs), filters, switched-mode power supplies, and power weapon systems [1]–[5]. Compared to ceramics and electrolytic materials, polymer-based capacitors are attractive because they have low manufacturing cost and low dielectric loss. They can be used at high voltage due to high breakdown strength, and fail gracefully with an open circuit. In many of these devices and systems, capacitors constitute a substantial fraction of volume and weight (> 30% volume and weight) [1]–[5]. To meet the demand of continued miniaturization of modern electrical and electronic devices and systems, the energy density of dielectric polymers must be improved. In general, the energy stored in a capacitor is proportional to the dielectric constant and the square of the electric field. Therefore, the materials of interest should display high dielectric constant and high breakdown strength. At the same time, these materials should exhibit low loss and high temperature stability. In this pursuit, our research group has developed a class of strongly dipolar polymers, urea and thiourea, with high dipole moments of 4.5 and 4.89 Debye respectively, with weak coupling among dipoles. These materials possess high dielectric constant and high breakdown strength while maintaining low loss [6].

Background and state of the art

The present state-of-the-art high energy density film capacitors use biaxially oriented polypropylene (BOPP). It is attractive for energy storage and regulation applications, such as capacitors in HEVs and power grids due to its high dielectric breakdown strength (700 MV/m) and low dielectric loss (< 0.018%). However, its low dielectric constant (K=2.2) limits its energy storage capability. In addition, the operating temperature is below 100 °C, due to its low melting temperature (T_m<140 °C) [3]. The conduction loss also becomes more significant at higher applied fields in BOPP as shown in Figure 1 [7,8]. The glass transition temperature (T_g) of BOPP is -10°C. Above T_g, the segmental motions of polymer chains will facilitate charge hopping, resulting in an exponential increase in leakage current with the electric field, and cause ohmic heating of the capacitors [2,7-9]. This necessitates a cooling system to avoid overheating of the BOPP film capacitors. For example, in hybrid electric vehicles, an extra cooling loop has to be introduced in the BOPP capacitor banks in order to prevent a runaway temperature increase caused by the conduction loss heating.



(a)



(b)

Figure 1. (a) D-E loop of BOPP showing conduction loss, (b) Leakage current as a function of field. [taken from (7)]

The strongly dipolar polymers developed in the past years in my group, have a glass transition temperature (T_g) above 150°C, which makes them a good candidate for high temperature operations. For example, aromatic polyurea (ArPU) has a glass transition above 200°C. The high dipole moments in these amorphous polymers provide strong polar-scattering centers and traps, which significantly reduces the conduction loss at high electric fields. As a result, these polymers exhibit an improved electrical energy density relative to BOPP.

However, conduction losses become prominent at temperature above 140°C [10] for these polymers, as shown in Figure 2. This raises a critical question — why are these losses occurring at temperatures below T_g? Similar trend is observed in the class of aromatic polythioureas.

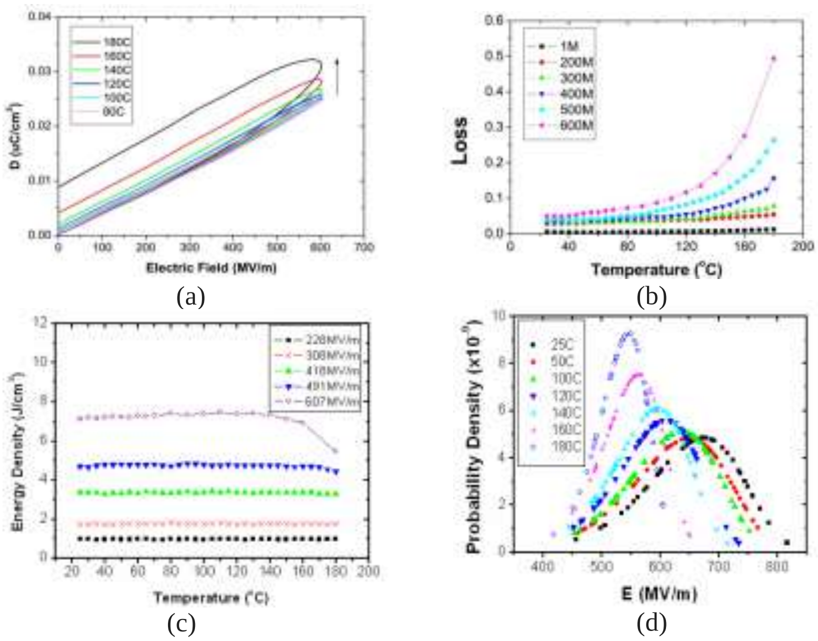


Figure 2. (a) D-E loop of ArPU, (b,c) Loss and energy density calculated from D-E loop as a function of temperature, (d) Weibull distribution of ArPU film at different temperatures.

In dielectric polymers, there are two main approaches which have been studied extensively to mitigate the charge injection and conduction losses: 1) nanocomposite fillers, 2) charge blocking layer at the metal-dielectric interface. This study will focus on investigating the effect of nanocomposite to mitigate conduction losses in the strongly dipolar polymers developed. It has been shown that inorganic fillers like zinc oxide (ZnO) [11,12], alumina (Al_2O_3) [13] and magnesium oxide (MgO) [14] introduce deep traps in the polymer matrix, thus reducing the charge transport by trapping the carriers. The nanocomposites have a large specific surface area, and that leads to large amount of interface areas between the nanoparticles and the polymer matrix. It has been shown that the polymer molecules in the interface areas are partly immobilized due to their interaction with the nanoparticles and the steric hindrance of the nanoparticles. The change in the local structures of the interface polymers may increase the density and depth of the charge carrier trapping sites [15-17]. It has also been seen that the breakdown strength increases with appropriate amount of nanofiller loading [13,14].

Proposed work

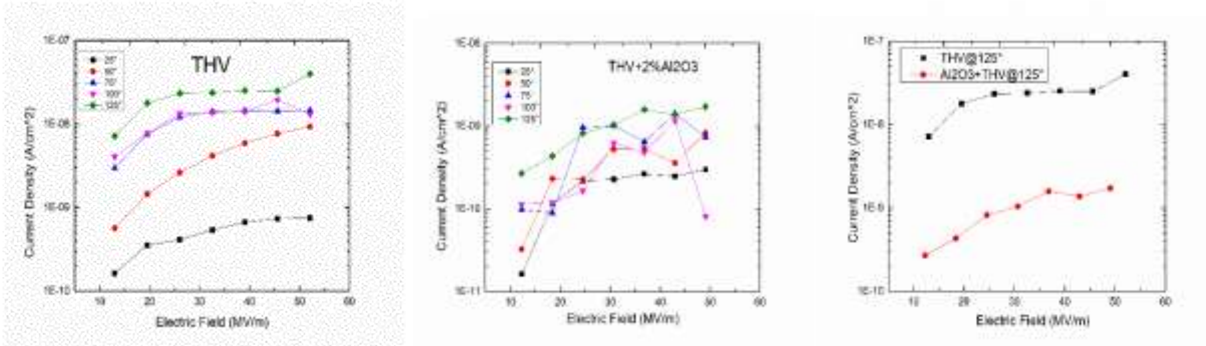
The aim of this study is to understand the conduction mechanism at high temperatures and high fields in strongly dipolar polymers. At the same time, provide a potential solution to mitigate the conduction losses, i.e. by adding nanocomposites to the polymer matrix. In this pursuit, we are collaborating with Dr. Meng H. Lean (CTO of QE Done LLC), who has developed dynamic charge mapping models capable of simulating bipolar charge transport in both layered and nanocomposite films. I plan to carry out the DC and AC conduction current measurements as well as trap analysis on these polymers. At the same time, I want to study the effect of nanocomposite on an industrial grade polymer. I plan to work with a semi-crystalline polymer – poly (tetrafluoroethylene hexafluoropropylene-vinylidine fluoride) (THV) terpolymer. The pure polymer results have been published and are reproducible by experiments [18]. Alumina nanocomposites have been selected as a material of choice because of their excellent insulating and thermal characteristics. Different composition of nanocomposites will be investigated to find the optimum percentage of nanocomposites required and their effect on the microstructures of the polymer will be studied. I also plan to carry out a high spatial resolution space charge distribution study to gain an insight into the space charge accumulation in the bulk polymer under applied field. Therefore, combined theoretical and experimental study will provide a better understanding of reducing charge conduction using trapping in these materials, which will lead to development of high temperature polymer based dielectrics with high energy density and low loss.

Sample preparation and experiments

The THV polymer crystals have been provided by PolyK Technologies, LLC. The crystals are processed in a twin screw micro compounder and then the polymer films of thickness 30-40 µm are hot pressed at 300°C. The thickness of the film was measured by alpha-step profilometer. Alumina nanoparticles of size 30-50 nm dispersed in IPA, are mixed with the polymer crystals by weight percent and dried in vacuum oven till the solvent dries. It undergoes the same processing as pure polymer for obtaining the film. Gold contacts of 5 mm diameter are deposited on the film samples. The current is measured using the HP 4140B pA meter/DC voltage source which is connected to Trek High voltage Amplifier (Model 609 D-6) and environment test chamber (Delta 9023). Both room temperature and elevated temperature measurements of current are done using this setup.

Work plan and experimental facilities

The experimental work for high field conduction study has just started and effect of alumina nanocomposites is being studied on THV polymer. The preliminary results look promising and suggest that the use of nanocomposites is an effective solution to reduce the conduction loss. The current as a function of electric field at different temperature for pure THV polymer and with 2% of Al_2O_3 by weight was measured, as shown in Figure 3. The Figure 3 (c) shows that the conduction current at 125°C is reduced by more than an order of magnitude by addition of Al_2O_3 nanofillers.



(a) (b) (c)

Figure 3. Plot of current density as a function of electric field at different temperatures for (a) THV, (b) THV+2% Al2O3 (c) comparison of both polymers at 125°C.

The room and elevated temperature electrical measurements, such as conductivity measurements, polarization measurements and thermally stimulated depolarization current measurements will be performed to measure the DC and AC conduction current as well as measure trap depths. Simultaneously, simulation studies will be carried out to study the conduction mechanism. I also plan to travel to China next year and carry out a high spatial resolution space charge distribution study, which will be a collaboration with Prof. Y.W. Zhang group in Tongji University of China. Prof. Y.W. Zhang group at Tongji University has developed a sophisticated high spatial resolution space charge distribution measurement system.

Impact

For industrial applications, it is critical to reduce the leakage current at high temperature, close to 150°C at 100-200 V/um, which is a typical operating condition for advanced power conditioning capacitors. The study will provide a better understanding of charge conduction and use of nanocomposites as a potential solution to reduce conduction loss. This study will lead to the development of high temperature polymer-based dielectrics with high energy density and low loss.

References

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Summary of Research Contributions

Refereed journal articles:

[J1] Y. Thakur, R. Dong, M. Lin, S. Wu, Z. Cheng, Y. Hou, J. Bernholc, and Q. Zhang, "Optimizing nanostructure to achieve high dielectric response with low loss in strongly dipolar polymers," *Nano Energy*, vol. 16, pp. 227–234, 2015.

[J2] Y. Thakur, M. Lin, S. Wu, Z. Cheng, D.-Y. Jeong, and Q. Zhang, "Tailoring the dipole properties in dielectric polymers to realize high energy density with high breakdown strength and low dielectric loss," *J. Appl. Phys.*, vol. 117, no. 11, p. 114104, 2015.

[J3] Z. Cheng, M. Lin, S. Wu, Y. Thakur, Y. Zhou, D.-Y. Jeong, Q. Shen, and Q. Zhang, "Aromatic poly (arylene ether urea) with high dipole moment for high thermal stability and high energy density capacitors," *Appl. Phys. Lett.*, vol. 106, no. 20, p. 202902, 2015.

Refereed conference articles:

[C1] Y. Thakur, M. Lin, S. Wu and Q.M. Zhang "Introducing Free Volume in Strongly Dipolar Polymers to Achieve High Dielectric Constant", paper accepted for *IEEE CEIDP* 2015.

[C2] A. Sabeeh, Y. Thakur, J.-H. Chao, A. Kshirsagar, and J. Ruzyllo, "Methods of Patterned Mist Deposition of Nano-Crystalline Quantum Dot Films," *ECS Trans.*, vol. 64, no. 43, pp. 1–5, 2015.

Conference Travel

I hereby affirm that, as an Indian citizen on F1 student visa in US, visa issues will not be an impediment for travel to a DEIS-sponsored conference or to the next CEIDP.