

**Polymer Nanocomposites as Future Materials for Defense and Energy Applications:
High Energy Density Storage Systems with Reduced Size and Weight for Pulse
Power Applications**

Hans-Conrad zur Loye, Department of Chemistry and Biochemistry
Harry J. Ploehn, Department of Chemical Engineering
University of South Carolina

The objective of our research is to combine high dielectric constant platelet materials and high breakdown voltage polymers to yield polymer-platelet composites with an improved overall dielectric-constant / breakdown-voltage combination. These polymer nanocomposite dielectric materials will be used to prepare high-energy storage capacitors useful for pulse power applications. The approach we have taken is to synthesize high permittivity inorganic platelet materials, covalently functionalize the platelet surfaces with organic groups, and prepare polymer nanocomposites incorporating these materials. We pursued the preparation of new metal phosphonate based polymer composites and measured their energy densities at various temperatures. Specifically, using nano-Ti(PPA)₂, the energy densities were up to 3.7 J/cm³ at 20 °C; 3.6 J/cm³ at 150 °C; and 1.6 J/cm³ at 275 °C.

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Sol-Gel CCTO/P(VDF-HFP) Composites with High Energy Density

During the previous reporting period we found that CCTO ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) synthesized via a novel sol-gel method leads to polymer composites with dielectric constants (ϵ_r) and theoretical energy densities much higher than composites containing CCTO synthesized by the standard solid-state route. At the optimal 20 vol% CCTO loading, our CCTO-P(VDF-HFP) composite has $\epsilon_r \sim 82$ at 1.0 kHz, high breakdown field strength (~ 200 MV/m), and a theoretical energy density of 14.5 J/cm^3 at room temperature. This value is three times the theoretical energy density of the neat polymer (4.5 J/cm^3) based on measured values of ϵ_r and breakdown field strength (10.6 and 310 MV/m). Ceramics such as BaTiO_3 or $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) have high dielectric permittivities, but they suffer from very low breakdown field strength and thus low stored energy density. In addition, they are brittle, so large area films are not mechanically robust. Polymers, on the other hand, are readily processed into high-area films with good mechanical properties, thermal tolerance, and high breakdown field strengths. Thus polymers and polymer composites offer the promise of high density dielectric energy storage if we can identify optimal compositions that achieve high offer high dielectric permittivity and high breakdown field strengths. Copolymers such as P(VDF-TrFE) have ϵ_r values as high as 50 upon conversion into a relaxor ferroelectric. The terpolymer, P(VDF-TrFE-CTFE), has an even higher $\epsilon_r \sim 65$, and an energy density of $\sim 13 \text{ J/cm}^3$ based on the measured values of ϵ_r and breakdown field strength of about 500 MV/m. Unfortunately, these copolymers suffer from high dielectric loss values and cannot be used at elevated temperatures.

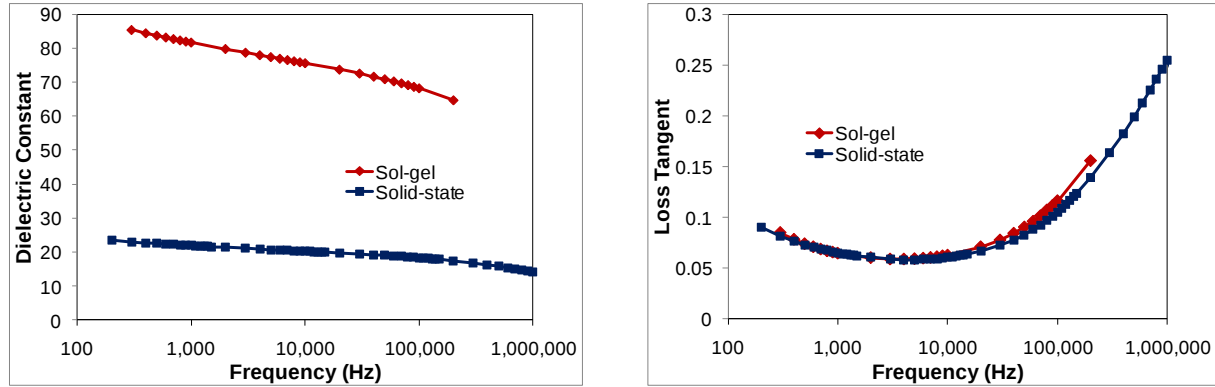


Figure 1. Dielectric constant and loss tangent of CCTO/P(VDF-HFP) composite films containing 20 vol% of sol-gel CCTO or 20 vol% solid-state CCTO.

High Dielectric Polymer Composite Materials from a Series of Mixed Metal Phenylphosphonates, $\text{ATi}(\text{C}_6\text{H}_5\text{PO}_3)_3$ for Dielectric Energy Storage

In addition, we looked mixed metal phosphonate based composites, where we developed a new synthetic route to mixed metal phosphonates. The results from the polystyrene-based composites was promising and resulted in good dielectric constants for various weight loadings.

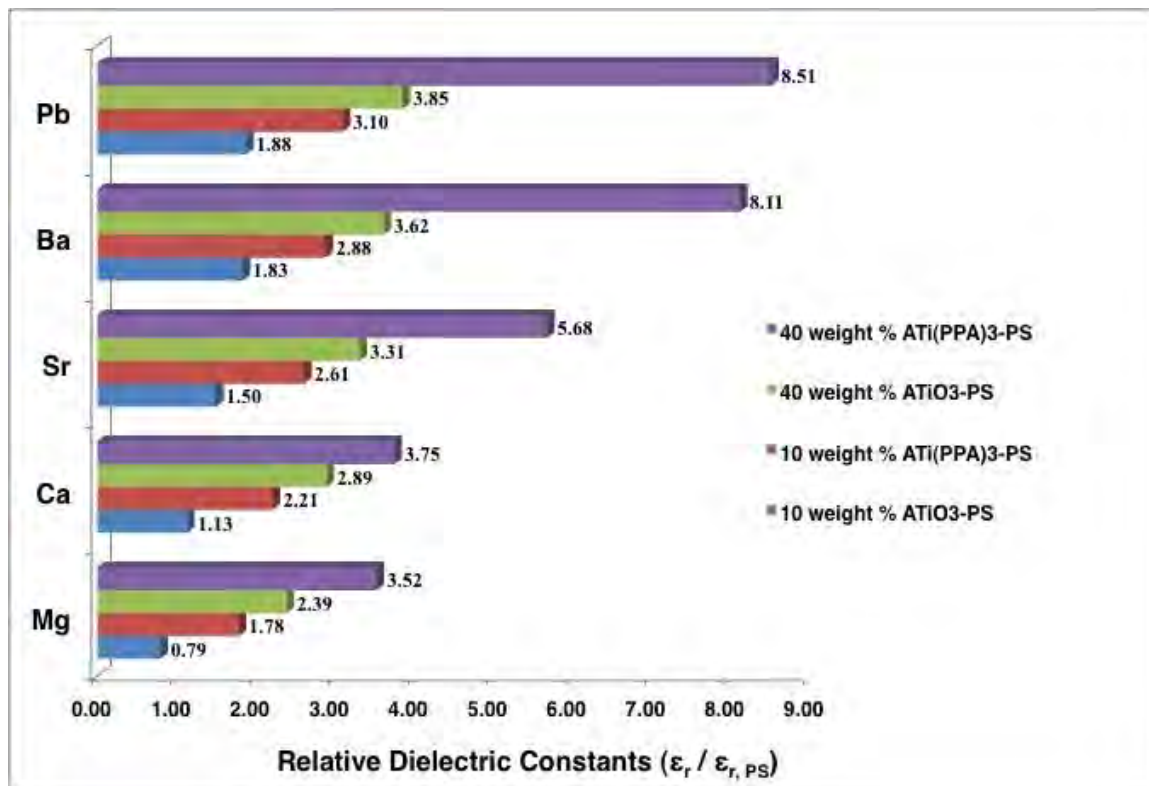


Figure 2. Relative dielectric constants for the ATiO₃-PS and ATi(PPA)₃-PS composites.

Since this work generated very promising results it was continued during this reporting period. We collaborated with Dr. Rob Klein from Luna Innovations. A paper summarizing this work has been submitted for publication to IEEE TDEI.

In this manuscript we reported that polymer nanocomposites utilizing nanoscale, covalently modified organo-platelets (CMOP) can lead to significantly increased breakdown field and material energy density. These materials also have the potential to be easily incorporated into existing solution casting or extrusion manufacturing processes for polymer film capacitors, leading to low cost devices with significantly enhanced breakdown field. These nanocomposites are especially promising for wide-temperature use, with the potential to operate from room temperature to 300 °C.

At conventional operating temperatures (<90 °C), metalized polymer capacitors have significant advantages over their ceramic, electrolytic, and glass counterparts, including

mechanical durability/flexibility, high energy density, and self-clearing/graceful failure. There are recent technologies in the ceramic and glass capacitor arenas that offer mechanisms for graceful failure, but these are typically costly to engineer and manufacture. Polymer film capacitors also do not typically suffer from ferroelectric and piezoelectric transitions (PVDF-based ferroelectrics are exceptions) which will adversely lead to large changes in capacitance and electrode debonding when operated over wide temperature ranges. Moderate to high temperature polymer film capacitors that are produced on a commercial scale include polypropylene, polycarbonate, polyphenylene sulfide, polytetrafluoroethylene, and polyimides/fluorene polyester. These materials offer operating temperatures from -25 to high as 85 °C, 125 °C, 150 °C, 200 °C, or ~ 300 °C, respectively. Polyimides (PI) and fluorene polyester (FPE) are the most recent additions to be produced in metric ton quantities. Ceramic capacitors can handle higher temperatures, but are typically limited to a 100 °C window where a $\pm 5\%$ capacitance rating is achieved. Despite these difficulties, there has been moderate success in incorporating low-dielectric constant fillers into polymer film capacitors, with increases in the energy density primarily occurring through increases in the breakdown field.

Surface modification to the filler can lead to significantly improved dispersion as well as decreased concentration of the electric field at interfaces, thereby resulting in a higher breakdown field. In particular, modified ceramic particles where the organic group is covalently attached to the surface (covalently modified organo-platelets, or CMOP), offer significant benefits over conventional modifications where the organic group is bound to the inorganic surface through electrostatic, dipolar, or hydrogen-binding interactions. During polymer/filler processing, the CMOP approach prevents physically segregation of organic modifying species, which would favor platelet re-aggregation. Charged surfactants that favor avalanche breakdown are also avoided.

The single and mixed metal phosphonates provide a family of CMOP-type materials with covalently attached surface groups. The zur Loye group pioneered the synthesis of the mixed metal phosphonates and has used them successfully in composites. Particles are synthesized as high aspect ratio stacks that are fully functionalized by layers of phosphonate. As the platelets can be synthesized in a single step with nano-scale dimensions, a high aspect ratio, and inherently functionalization, production costs are therefore significantly reduced. These layered materials can also exhibit excellent wide-temperature performance. Barium titanate phenyl phosphonate (BaTi(PPA)_3) and titanium phosphonate (Ti(PPA)_2) display no measurable Curie transitions or significant changes in dielectric constant with temperature, as measured by differential scanning calorimetry and impedance spectroscopy with temperature. This is in contrast to

barium titanate, which possesses a strong Curie transition at 120 °C. Additionally, BT(PPA)_3 and Ti(PPA)_3 are stable by thermal gravimetric analysis up to 400 °C, which is exceedingly high for an organically functionalized nanomaterial. The in-plane and out-of-plane structures of $\text{Ti(C}_6\text{H}_5\text{PO}_3)_2$ are shown in Figure 3.

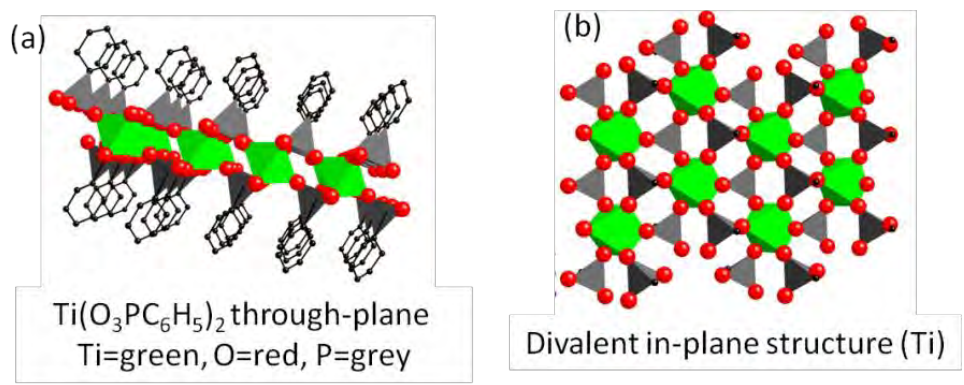


Figure 3. Arrangement of atoms in Ti(PPA)_2 : (a) the arrangement of Ti, O, P, and phenyl groups and (b) in-plane structure of Ti(PPA)_2 .

SEM images of Ti(PPA)_2 , synthesized at various temperatures, are shown in Figure . Particle dimensions decrease with synthesis temperature. The particles shown in 4(c), which were the smallest synthesized and separated in this study, also led to the highest performing nanocomposite films. The FESEM image in 4(d) provides slightly improved magnification. Based on the particles shown in this and similar images, it is estimated that 90% of the particles have diameters between 100 and 250 nm and thicknesses between 5 and 10 nm; the aspect ratio ranges from 10 to 50.

Ball milling of micron-scale Ti(PPA)_2 has been investigated previously as a route to produce nano-scale particles. However, ball milling uniformly reduces all dimensions of the particles, therefore reducing the benefits of the platelet morphology.

The synthesis and characterization of micron-scale titanium phenyl phosphonate ($\text{Ti(C}_6\text{H}_5\text{PO}_3)_2$ or Ti(PPA)_2) platelets, where PPA=phenyl phosphonate, have been described in detail in our previous report. In the present investigation, nanoscale $\text{Ti(C}_6\text{H}_5\text{PO}_3)_2$ (nano- Ti(PPA)_2) platelets were prepared by adding a slightly basic aqueous solution of the titanium source ($\text{K}_2[\text{TiO(C}_2\text{O}_4)_2]$) drop-wise into a slightly basic aqueous solution of excess phenyl phosphonic acid. The first solution (A) consisted of 50 ml water, 1×10^{-4} M KOH, and 2.12 g $\text{K}_2[\text{TiO(C}_2\text{O}_4)_2]$ (6 mmol). The second solution (B) consisted of 200 mL water, 1×10^{-4} M KOH, 3.16 g phenylphosphonic acid (20 mmol).

Three types of Ti(PPA)_2 were generated by changing the temperature of the first and second solutions: (1) solution A at 5 °C, solution B at 100 °C; (2) solution A at 20 °C, solution B at 20 °C; and (3) solution A at 5 °C, solution B at 20 °C. Method (3) generated the smallest particles, as shown in SEM images. Additionally, it was found that chilling both solutions to 5 °C led to a completely clear solution, indicating that either particle growth was extremely slow at these temperatures, or particles were sufficiently small to for the solution to remain transparent.

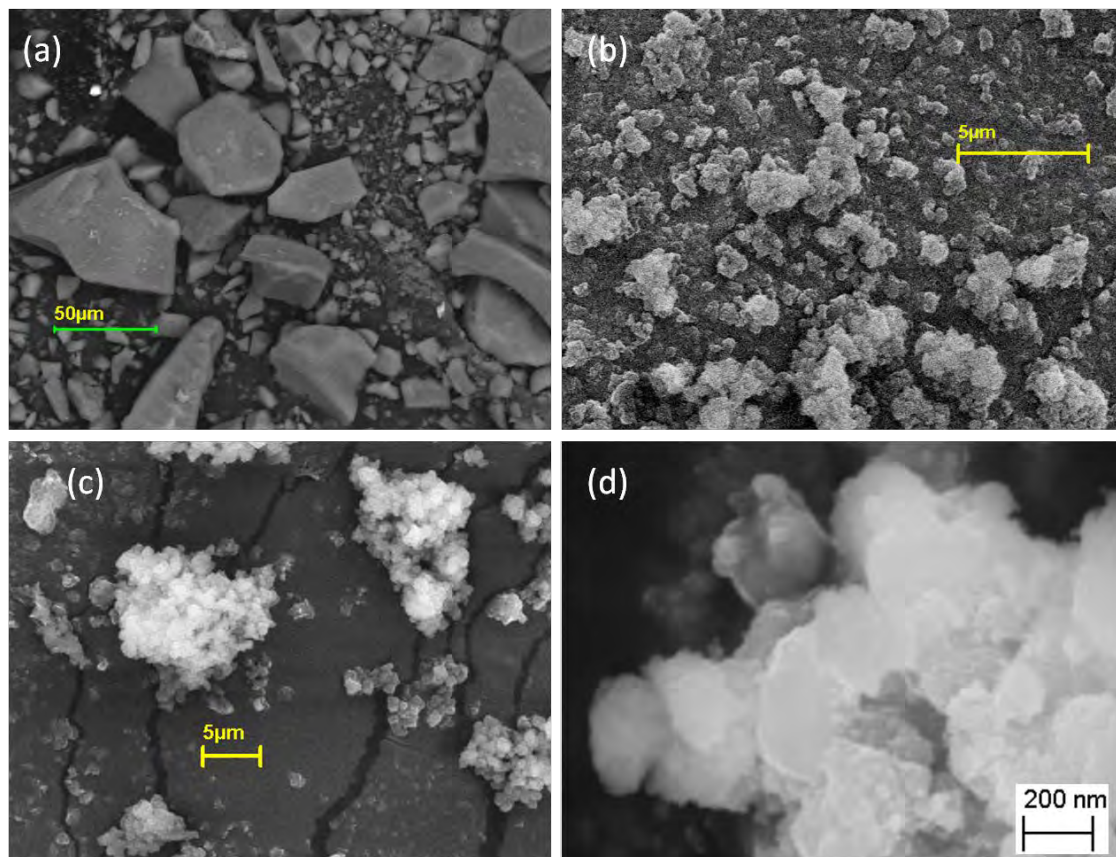


Figure 4. SEM images of Ti(PPA)_2 synthesized at various temperatures: (a) Ti source at 5 °C and PPA source at 100 °C; (b) Ti and PPA sources at 20 °C; and (c) Ti source at 5 °C and PPA source at 20 °C. (d) FESEM image of the platelets in (c).

Samples were characterized for chemical composition, purity, and size using a combination of powder x-ray diffraction, ^{31}P magic angle spinning nuclear magnetic resonance, thermal gravimetric analysis, ultraviolet-visible spectroscopy, differential scanning calorimetry, transmission electron microscopy, and atomic force microscopy.

SEM images were collected on a LEO 1430VP SEM operating at 25 keV. Field Emission SEM images were collected on a Zeiss Ultraplus Thermal FESEM operating at 7.8 keV.

Fluorene polyester (FPE) was obtained from Ferrania Technologies as a powder. According to the supplier datasheet, the polymer has a molecular weight of at least 300,000 g/mol, polydispersity index of ~ 7 , glass transition temperature of 330 °C, dielectric constant between 2.8 and 3.2, and breakdown field between 150 V/ μm and 430 V/ μm . Films were cast from low weight fraction solutions with methods designed to be scalable to continuous casting drums. Dilute polymer solutions, using dichloromethane as a solvent, were filtered with 1 μm Teflon[®] filters prior to incorporation of the filler. Filler was then dispersed into the solution with the aid of a horn sonicator with microtip attachment (Misonix 3000). Films were cast with no filler, 0.3 w% nano-Ti(PPA)₂, 1 w% nano-Ti(PPA)₂, and 3 w% nano-Ti(PPA)₂. Films were cast on 4"x6" glass plates and solvent was evaporated at 30 °C under partial pressure of the solvent. Films were then further dried at 60 °C for 4 h. Dry film thicknesses ranged from 5 to 7 μm , and 200 nm thick aluminum electrodes were evaporated onto masked films for impedance testing. Breakdown testing was performed on unelectroded film.

Nano-Ti(PPA)₂ filler shown in Figure (c)/(d) exhibited excellent mixing behavior with fluorene polyester at 0 to 3 w% of total solids. The dispersion of nano-Ti(PPA)₂ was excellent in low viscosity solvated polymer solutions as well as the resulting cast films. Films were optically clear and SEM of the film surfaces could not distinguish individual particles.

When measured across varying frequency (10 Hz to 100 kHz), loading level of nano-Ti(PPA)₂ (0 to 3 w%), and temperature (20 to 300 °C), the dielectric constant was between 2.6 and 2.8 with a standard deviation of ± 0.05 . Within experimental error, there was no significant change in the dielectric constant over these ranges. These materials exhibited a loss tangent (ϵ''/ϵ') between 0.006 and 0.01 at 20 °C, with a standard deviation of approximately 50%. The loss tangent was flat within experimental error from 20 to 250 °C. At 275 and 300 °C, the neat FPE exhibited a loss tangent between 0.01 and 0.03, and FPE loaded at 1 and 3 w% exhibited a loss tangent between 0.006 and 0.015, indicating the presence of the Ti(PPA)₂ led to a slight suppression of the loss tangent.

Breakdown fields were measured for films of neat FPE and FPE loaded with 0.3, 1, and 3 wt% nano-Ti(PPA)₂. For each composition and temperature, 20 to 25 samples were measured. Data were fit by the two-parameter Weibull relation for cumulative probability of failure, as presented in Figure 5 for measurements taken at 150 °C. Upon

loading to 3 w% nano-Ti(PPA)₂, significant increases in breakdown field were observed at 20, 150, and 275 °C: 37%, 39%, and 18%, respectively. Breakdown field increased with loading level of Ti(PPA)₂ for these low loading levels; at some loading level this effect reaches a maximum, since 20 and 40 wt% Ti(PPA)₂ were found to exhibit much lower breakdown fields than neat FPE.

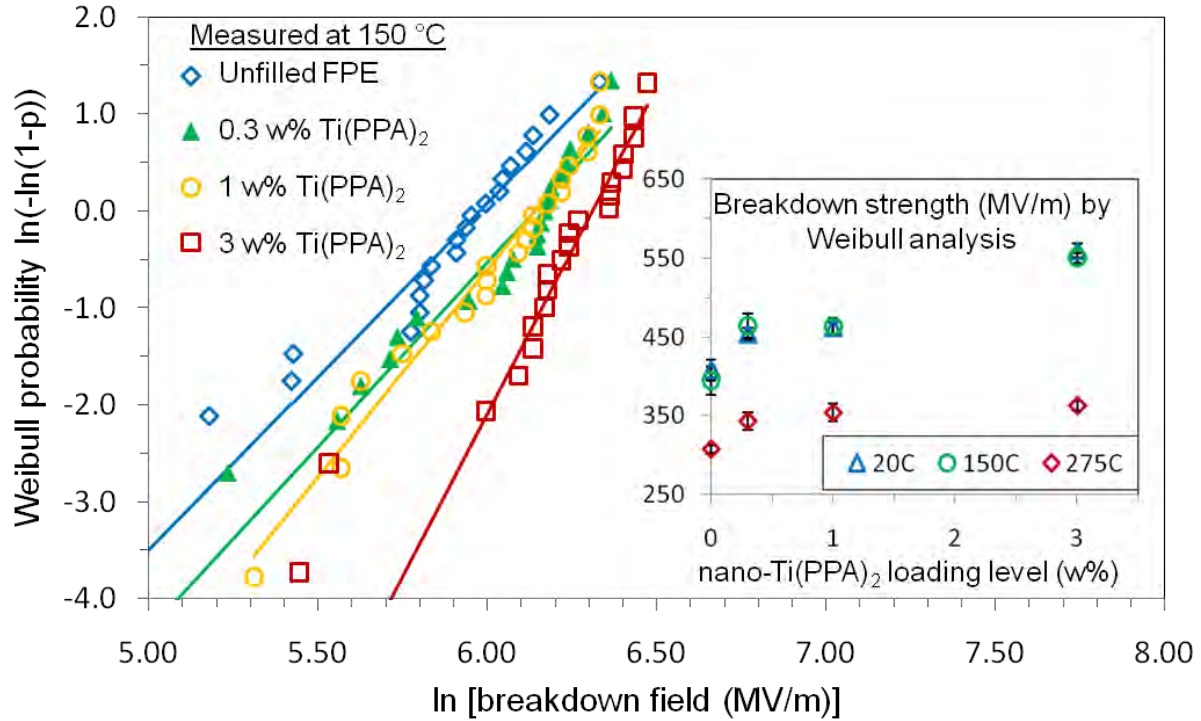


Figure 5. Weibull plot for the breakdown field of the four loading levels, as measured at 150 °C. Inset: Weibull breakdown strengths and 95% confidence intervals for 0 to 3 wt% loading with nano-Ti(PPA)₂ over the 20 to 275 °C temperature range.

The breakdown field in polymer composites typically decreases with the addition of filler particles due to (1) lower breakdown field of the filler, (2) concentrated electric field at the polymer-filler interface, and/or (3) water or ionic species introduced with the filler. Condition (2) occurs due to a discontinuity in the dielectric constants and conductivities at interfaces between different materials, and this increases the probability of a current path percolating through the matrix along pathways that intersect the interfaces. The effect is typically observed when barium titanate or similar high dielectric constant filler is incorporated into the polymer matrix, leading to significant decreases in breakdown field. Condition (3) is often observed in neutral or ionic fillers that require surfactants to improve dispersion, such as with clay-based fillers. With the low volume fraction of filler used here, it is highly unlikely that the composite modulus was increased over the neat polymer. Therefore, the enhancement

in breakdown field most likely arises from a decreased conductivity, due to the barrier properties of the filler, or from decreases in free volume and voids in the polymer matrix.

Material energy densities were calculated from a dielectric constant of 2.7 and breakdown fields determined from the Weibull analysis breakdown fields. For 0 and 3 w% loading with nano-Ti(PPA)₂, the energy densities were, respectively, 2.0 and 3.7 J/cm³ at 20 °C; 1.9 and 3.6 J/cm³ at 150 °C; and 1.1 and 1.6 J/cm³ at 275 °C. Therefore, enhancements in energy density upon loading with 3 w% Ti(PPA)₂ reached 88%, 95%, and 39% at 20, 150 and 275 °C, respectively.

In fully assembled polymer film capacitors, the safety/packing factor is approximately 1/4 to 1/2. Therefore, capacitors utilizing FPE loaded with 3wt% nano-Ti(PPA)₂ and operating below 200 °C would exhibit an energy density between 0.7 and 1.9 J/cm³. At temperatures between 200 to 275 °C, the capacitor energy density would fall between 0.3 and 0.8 J/cm³. Commercially available polymer capacitors with maximum operating temperatures of 140-200 °C, such as those based on polycarbonate, are typically rated to 0.1-0.5 J/cm³.

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Future potential: Our conclusions at the end of this project are that the breakdown voltage and dielectric loss can potentially be improved by tethering the platelets to the polymer. Specifically, work aimed at growing polymer chains off the surface of platelets, which can be done via RAFT techniques, can lead to fewer interfaces and defects in the structure leading to improved breakdown voltages and lower dielectric loss. We would expect that such work would yield capacitors with substantially higher energy densities. We recommend that such work be undertaken in the future.

During the last few months we investigate the preparation of ferroelectric organic inorganic hybrid structures for incorporation into the polymers to create new composites. While the work was started and resulted in the synthesis of a large number of new structures, their structure determinations and an investigation of their properties, there was not enough time to create composites. The structural portion of this work has been published and the references are listed in the afosr-report.