

Center for Energy Harvesting Materials and Systems

The CEHMS Chronicle

Technical Article: Enhanced Piezoelectric Performance

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- Don't forget to sign up for the [2013 Energy Harvesting Workshop](#), July 14-18 in Hannover, Germany!
- Next [IAB meeting](#) will take place in Hannover, Germany in July.

Inside this issue:

Technical Article	2-4
Laboratory Highlight	5
International Relations	5
Student Highlight	6

Enhanced Piezoelectric Performance from Carbon Fluoropolymer Nanocomposites

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With the use of microsensors, transmitters and personal electronics growing daily, there is a growing need for longer lasting, more efficient power sources. In recent years, researchers at CEHMS have made great strides toward this goal through the development of novel, efficient energy harvesting materials and systems. The concept of "energy harvesting" is the capture and use of environmental energy to power a device. Among wasted sources, vibrational energy is perhaps the most readily available, and can be captured through the use of piezoelectric materials. Piezoelectric materials experience a net distortion of charge when stressed from the equilibrium position, resulting in the flow of electricity.²

The two classes of piezoelectric materials that are commonly used for vibrational energy har-

vesting are polycrystalline ceramics and polymers. While ceramics exhibit large piezoelectric coefficients with high electromechanical coupling, stiffness and low processability limit their range of vibrational harvesting and integration into small devices. Polymers offer greater elastic compliance and processability than ceramics, allowing for a broader range of vibrational harvesting and easier device integration. However, the piezoelectric output of polymers is much lower than ceramics due to their low charge capacity and dielectric storage, greatly limiting their integration into energy harvesting devices.

In recent work, we have demonstrated that the d_{31} strain coefficient of PVDF can be doubled through the controlled incorporation of carbon fullerenes (C60) and single-walled carbon

nanotubes (SWNT). The composites were optimized for Young's modulus, dielectric constant, increased internal charge, and ultimately, the d_{31} piezoelectric coefficient. The electromechanical coupling coefficients (k_{31}) at optimal loading levels were found to be 1.84 and 2 times greater than pure PVDF for the PVDF-C60 and PVDF-SWNT composites, respectively. Such composites combine both large piezoelectricity with the natural compliance and sensitivity of polymers, and may significantly benefit vibrational energy harvesting technology.

The charge being introduced to PVDF with the addition of nanoparticles can be quantified through Thermally Stimulated Current (TSC) testing. A typical TSC cycle involves first applying an electrical field to the sample followed by

Technical Article Cont.: Enhanced Piezoelectric Performance

heating at a steady rate and observing the release of charge. In this manner, a profile of charge release vs. temperature is obtained that can elucidate the depth and nature of the internal charge. Figure 1 shows the (TSC) charge release of the C₆₀ and SWNT PVDF nanocomposites relative to pure PVDF. Four dominant peaks are observed, two corresponding to the relaxation of polarized dipoles and two due to trapped charge in the material.³

The first peak, P₁, can be

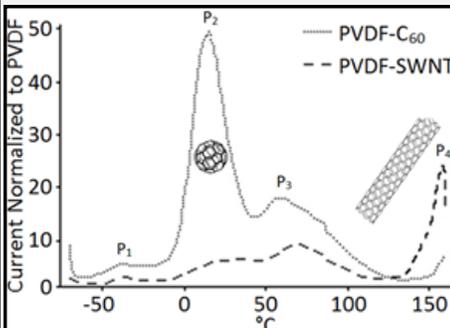


Figure 1. TSC spectra of 0.1 wt% PVDF-SWNT and PVDF-C₆₀

attributed to the depolarization of dipoles in the amorphous region due to relaxation back to the energetically-favored random orientations. The P₂ peak corresponds to the release of subsurface interfacial charge from the material. The C₆₀ composite shows a sharp, intense P₂ peak from 0-40 °C that is nearly 50 times greater than that of pure PVDF, while the SWNT composite shows a less intense peak that is 6 times greater. C₆₀, the more symmetric of the two nanoparticles, allows for a homogenous nanocomposite with a vast number

of small uniformly dispersed, low activation energy interfacial charges that are readily mobilized through charge hopping. The SWNT composite shows a less intense P₂ peak due to greater overlap between nanoparticles, that create low resistance pathways allow-

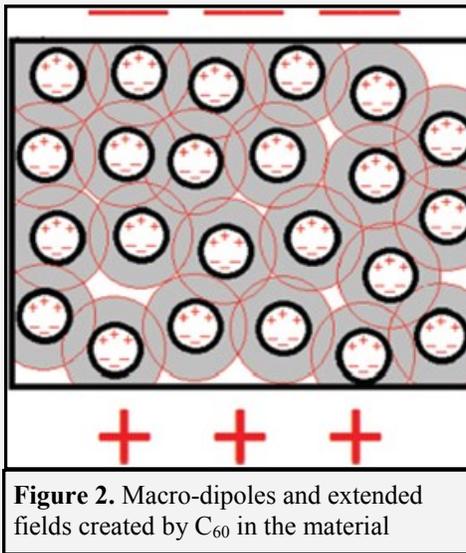


Figure 2. Macro-dipoles and extended fields created by C₆₀ in the material

ing charge dissipation.

The P₃ peaks roughly correspond to the Curie point of the composites. This is the temperature at which all polarization in the crystalline regions of the polymer is lost and the charges are released. The C₆₀ and SWNT composites show P₃ peaks roughly 18 and 9 times greater than pure PVDF, respectively. A larger release of current at the Curie temperature indicates a more efficient polarization of dipoles in the material. This is reasonable considering delocalization of electrons in both C₆₀ and SWNTs may produce 2X local field enhancements when under an electrical field, resulting in an extension of the effective poling radius (Figure 2).⁴ The delocalized electrons of both C₆₀ and SWNT are stabilized by the sur-

rounding dipoles, creating macro-dipole sites, increasing charge density. The final peak, P₄, beginning around 150 °C, corresponds to the flow temperature of the polymer. Upon melting, the remaining high activation energy charges are liberated from the material. Due to natural inhomogeneity, the SWNT composite contains a large amount of charge trapped at deep levels which are released upon melting (25 times), while the C₆₀ composite has less charge remaining (7 times PVDF).

Polarization vs. electric field (PE) curves are essential for validating a material's ferroelectric behavior at a particular temperature and frequency. When placed in a dynamic field environment, the dissipation of energy from the material produces a phase separation between the charge and voltage signals, giving a loop with a definable area under the curve. This area is an indication of the charge storage capability of the material, with a strong ferroelectric material exhibiting a large square curve quan-

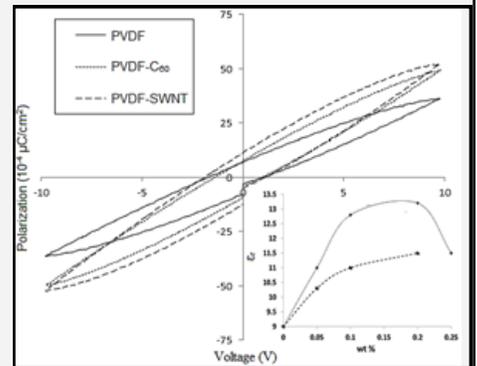


Figure 3. PE Hysteresis loop of pure PVDF, PVDF-C₆₀ (0.1 wt%), PVDF-SWNT (0.1 wt%). Inset dielectric constant (ϵ_r) profiles vs. Wt%

Technical Article Cont.: Enhanced Piezoelectric Performance

tified by remnant polarization and coercive field, and a lossy capacitor with a high $\tan\delta$ (dissipation factor) showing a narrow loop.⁵ In an ideal, voidless, ferroelectric polymer, we would expect that charge accumulation is due to the polarization of molecular dipoles. However, in a dielectric composite material, interfacial polarization (Maxwell-Wagner-Sillers polarization) develops due to a swell of charge at the inner dielectric boundaries of a conductively heterogeneous material, resulting in heteropolarization.⁶

Figure 3 shows a PE loop of the composites at a voltage of ± 10 V. An open curve is observed that only can be caused by internal heterogeneous charge. Pure PVDF shows a small amount of internal charge due to voids and impurities, but a significant increase in area and slope for both of the nanocomposites is measured. The shape and field sensitivity of these curves looks much like an electretic material curve. The area under this curve increases with loading percentage as expected from past results, but is naturally limited by conductivity at high loading levels. The increase in the magnitude of remnant polarization is indicative of the fact that molecular dipoles are able to align with the applied electric field. We also observe a shift towards the left axis for the hysteresis loops which is typically indicative of the internal bias field formed due to presence of defect dipoles. In our case, the bias field can be traced to the net ordering of

the interfacial charges as discussed in Fig. 2.

The instantaneous slope of the hysteresis curve yields the material's permittivity ($\epsilon_0\epsilon_r$), where ϵ_r is the relative permittivity and ϵ_0 is the vacuum permittivity (8.85 pF/m).

Shown in Figure 3, there is an increase in ϵ_r to 11.5 at 0.2 wt% for the SWNT samples, which are conductive above this level. The C_{60} composites show a larger increase in ϵ_r to a maximum of 13.2. A slow decrease in ϵ_r is observed in the C_{60} composites after the maximum as opposed to the sharp deterioration in the SWNT samples. The spherical shape of C_{60} allows for a higher loading level without conduction through the samples because there is a lower overlap between nanoparticles at a given loading level. Four point probe conductivity measurements revealed that at a loading level of 0.1%, the SWNT composite was 300% more conductive than the C_{60} composite, however, the difference jumped to 1000X at 0.25 wt%.

Table I shows the relationship between nanoparticle weight percentage and Young's modulus (Y). Pure PVDF exhibits a modulus of 1200 MPa, upon the addition of 0.05 wt% SWNT, the modulus increases to over 1300 MPa with a maximum of 1350 MPa at 0.1 wt%. The increase in

Table I. Young's Modulus (MPa) values

wt%	0	0.05	0.1	0.2	0.25
C_{60}	1220	1310	1400	1560	1400
SWNT	1220	1325	1355	1320	-

Young's modulus from the addition of SWNTs is limited by entanglements

and inhomogeneities. The C_{60} composites, however, have a lower increase in modulus with loading level but a higher maximum value in excess of 1550 MPa.

Piezoelectric enhancement was validated through d_{31} testing. Commercially produced, stretched and poled PVDF was tested as a control showing a d_{31} of 31.5 pC/N. As shown in Table II, the SWNT composites reach a maximum d_{31} of 65 pC/N at a loading level of 0.05

Table II. d_{31} (pC/N) values

wt%	0	0.05	0.1	0.2	0.25
C_{60}	32	36	44	63	59
SWNT	32	65	62	54	NA

wt% while the C_{60} composites reached a maximum d_{31} value of 63 pC/N at 0.2 wt%. Pure PVDF samples made in the same manner as the composites show a d_{31} of 32 pC/N.

While the d_{31} coefficient provides insight into the charge generated per unit applied force, the electro-mechanical coupling factor, k , is a measure of the efficiency of energy conversion, and can be expressed as:

$$k_{31} = \frac{d_{31}}{\sqrt{\epsilon_0\epsilon_r S_{11}}}$$

Where k_{31} is the coupling coefficient, ϵ_r is the relative dielectric constant and S_{11}^E is the compliance (inverse Y).⁷ This relationship is somewhat intuitive in that one would expect a stiffer material to experience larger strains, resulting

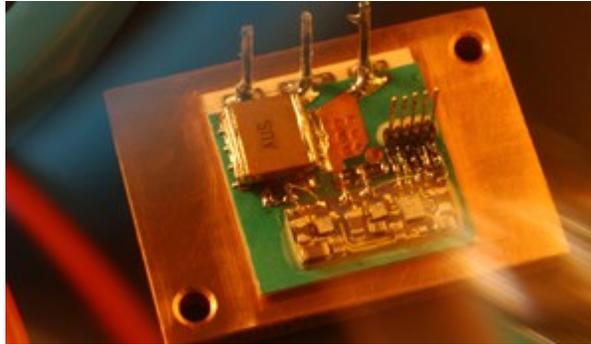
Technical Article Cont.: Enhanced Piezoelectric Performance

in larger internal mechanical energy. Also, while increasing the dielectric constant allows for a greater amount of charge generation, it also increases the force needed to move charge, resulting in a lower efficiency. If one assumes a constant d_{31} , the k_{31} is proportional to the square of the Y and inversely proportional to ϵ_r . Thus, one then would expect that by increasing the Y and decreasing ϵ_r , a very electromechanically-efficient material can be realized. However, it is impossible to change only one variable. For example, as Y is increased through the addition of the nanoparticles, ϵ_r generally increases due to the creation of dielectric boundaries, resulting in a performance tradeoff. According to literature, pure PVDF has a k_{31} of 0.12, and when calculated using the values measured here a k_{31} of 0.125 is obtained for PVDF.⁸ The maximum k_{31} for the C_{60} composites occurs at a loading level of 0.2 wt with a value of 0.23; 1.84 times that of pure PVDF. The maximum for the SWNT occurs at a loading level of 0.05 wt% with a value of 0.25, a value 2 times that of pure PVDF.

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Laboratory Highlight: Center for Power Electronics Systems (CPES)

The Center for Power Electronics Systems, headquartered at Virginia Tech, is a collaboration of five universities and many industrial firms. Started as a power electronics program called PERG (Power Electronics Research Group) at Virginia Tech in 1977, the group now includes University of Wisconsin-Madison (UW), Rensselaer Polytechnic Institute (RPI), North Carolina A&T State University (NCAT), and University of Puerto Rico-Mayagüez (UPRM). It was in 1998, that the Center was elevated to the national-level, as it became a National Science Foundation Engineering Research Center (NSF ERC), and named Center for Power Electronics Systems (CPES). The research vision is to enable dramatic improvements in the performance, reliability, and cost-effectiveness of electric energy processing systems by developing an integrated system approach via integrated power electronics modules (IPEM).



<http://www.cpes.vt.edu/public/aboutus/>

The state-of-the-art laboratory facilitates research spanning a plethora of sub-areas related to power electronics - from the micro-level study of materials for device packaging, to the macro-level study of high-power converters. Encompassing more than 19000 sq. ft., the research laboratory includes an electrical research lab, an integrated packaging lab, and a computer lab. It has upgraded its high power electrical research capability with the aid of a \$1 million DURIP grant. These rare advanced research capabilities help CPES maintain its leading position in power electronics.

With the annual research expenditures of \$4-5 million, the center currently constitutes of 7 faculty members, 5 research faculty members, and 41 graduate student members. The research done by the center since 1983 has resulted in over 3000 technical papers, theses and dissertations along with 79 patents awarded and 207 invention disclosures filed. The work at CPES focusses on five technology areas: (1) power conversion technologies and architectures; (2) power electronics components; (3) modeling and control; (4) EMI and power quality; (5) high density integration. The CPES industry consortium is a multi-tiered structure comprising of over 60 members. It provides an excellent interface between leading-edge companies and top-notch researchers.

International Relations: Delhi University

The University of Delhi is one of the leading universities in India and is recognized for its high standard of research and teaching. Since 1922, it has spread its root with 16 faculties, 86 departments, 77 colleges and at least 4,00,000 students all over the city. Active research can be found in various fields, from physics to bio-chemistry, soci-



ology to geography and economics to management studies. The Department of Physics and Astrophysics is one of the

established department in Indian Universities and provides an advanced level of post graduate teaching and re-

search. The research emphasis at The University of Delhi is on topics of condensed matter physics, nonlinear dynamics, plasma physics, high energy physics, nuclear & particle physics, nano-materials, string theory, semiconductors and much more.

Student Profile: Nathan Sharpes



Growing up on a farm in a very small town in VA, Nathan Sharpes found the transition to college life an easy one when he began his studies at Virginia Tech. “Despite my pursuit of an advanced engineering degree at the best technical college in Virginia, I feel very close to the farm and that simple way of life here in Blacksburg... My father, grandfather [etc.] were all farmers as far back as our ancestry can trace, so it was an easy transition for me to come to a University founded as an agricultural institution, located in a small town”.

While enjoying the rural atmosphere Virginia Tech offers its students, Nathan’s academic career has flourished, making him one of CEHMS’ top Graduate Researchers. His current focus is on “energy harvesting piezoelectric materials, and induction generators, powered by various sources, such as vibration, wind and human gait, as well as self-powered sensors.”.

With the knowledge Nathan has accumulated over his years of study and a background specializing in

piezoelectric materials, it was an obvious decision to include him in CEHMS. When asked about his experiences with working in an I/UCRC, Nathan could not have been more pleased with the opportunity and the advantages it supplies: “CEHMS is never far removed from its industry partners. As such, I am constantly exposed to the current and future pulses in industry. I believe this cooperation between academia and industry creates an environment where I can gain experience researching novel ideas, with the goal of an end product in mind, which is similar to what I hope to do in my career: working in research and development for a top company in industry... Which company and in what field, I am not yet sure”.

Well, one thing is for sure: this farmers’ son will successfully carry on his ancestors’ tradition of a career in harvesting. Just a different kind of harvesting.

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www.sites.me.vt.edu/cehms/

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