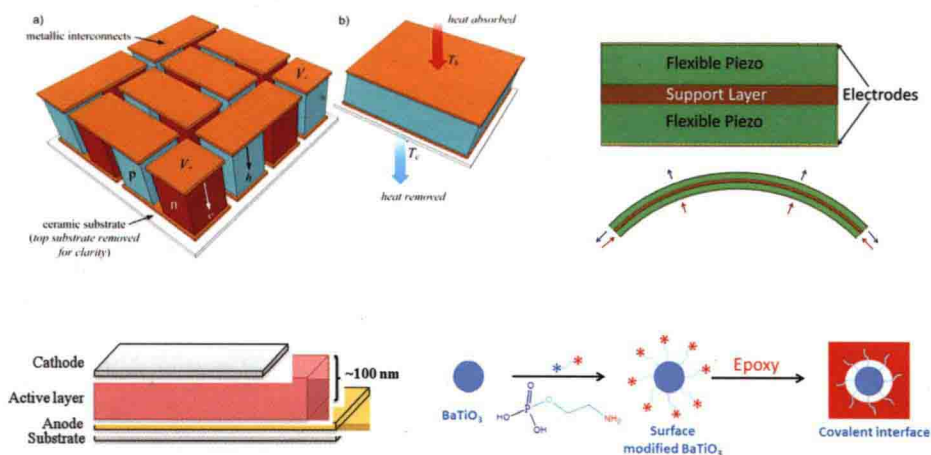


# Polymer Composites for Energy Harvesting, Conversion, and Storage



EDITED BY  
**Lan Li, Winnie Wong-Ng,  
 and Jeff Sharp**

ACS SYMPOSIUM SERIES 1161

# Polymer Composites for Energy Harvesting, Conversion, and Storage

**Lan Li**, Editor

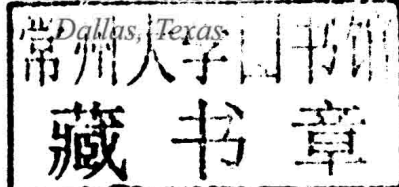
*Boise State University  
Boise, Idaho*

**Winnie Wong-Ng**, Editor

*National Institute of Standards and Technology  
Gaithersburg, Maryland*

**Jeff Sharp**, Editor

*Marlow Industries*



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# **Polymer Composites for Energy Harvesting, Conversion, and Storage**



# Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

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# Preface

The 245th American Chemical Society (ACS) Meeting and Exposition was held in the Morial Convention Center, New Orleans, Louisiana, on April 7–11, 2013. The ACS's meeting core theme was The Chemistry of Energy and Food. This proceedings volume contains articles that were presented at the symposium on Polymer Composites for Energy Harvesting, Conversion and Storage. The symposium has brought together experts from the different areas of polymer composite research to address the scientific, engineering, economic, environmental, and health issues involved in the production and use of polymer composites. The symposium has also provided a forum for researchers to introduce the high-performance, low-cost, and environmentally friendly polymer composites and techniques for energy applications into the marketplace.

Based on the symposium content, we invited the speakers to turn their symposium presentations and research work into 9 chapters for this proceedings volume. The volume explores polymer composites in terms of their chemical synthesis, characterization, and applications in the energy field, from photovoltaics to fuel cells, from thermoelectrics to energy harvesting and storage. The articles include state-of-art synthesis, characterization, and measurement techniques applied to polymer composites. Such methods addressed the key challenges involved in the processing of polymer composites, such as structural and morphological control, interface characterization, property optimization, and the identification of potential candidates for desired performance, etc. The order of the articles in the proceedings volume is different from that of their presentations at the meeting. This volume contains updates to existing polymer composite publications with the newest research work in energy applications, as well as reviews that present new evaluation and analyses of published research. In summary, all the articles in the proceedings volume reveal the latest research on polymer composites, and are available source material for researchers and managers working in this field.

The success of the symposium and the publication of the proceedings could not have been possible without the effort and support of the ACS and other organizers of the program. We acknowledge Mr. Tim Marney, Ms. Aimee Greene, and Ms. Arlene Furman for their involvement in editing and producing this book. Special thanks are due to the speakers, authors, manuscript reviewers, and ACS program coordinators and officials for their contributions.



**Lan Li, Ph.D.**

Department of Materials Science and Engineering  
Boise State University  
1910 University Drive  
Boise, ID 83725-2090  
lanli@boisestate.edu (e-mail)

**Winnie Wong-Ng, Ph.D.**

Materials for Energy and Sustainable Development Group  
Materials Measurement Science Division  
National Institute of Standards and Technology (NIST)  
100 Bureau Drive, Stop 8520  
Gaithersburg, MD 20899

**Jeff W. Sharp, Ph.D.**

Materials Research and Development Department  
Marlow Industries, Inc.  
10451 Vista Park Road  
Dallas, Texas 75238

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## Chapter 1

# Advances in Piezoelectric Polymer Composites for Vibrational Energy Harvesting

Cary Baur,<sup>\*,1</sup> Daniel J. Apo,<sup>2</sup> Deepam Maurya,<sup>2</sup> Shashank Priya,<sup>2</sup> and Walter Voit<sup>3</sup>

<sup>1</sup>Department of Chemistry, and The Alan G. MacDiarmid Nanotech Institute, The University of Texas at Dallas, 800 W. Campbell Road, Richardson, Texas 75080, U.S.A.

<sup>2</sup>Bio-inspired Materials and Devices Laboratory (BMDL), Center for Energy Harvesting Materials and Systems (CEHMS), Virginia Polytechnic Institute and State University, 310 Durham Hall, Blacksburg, Virginia 24061, U.S.A.

<sup>3</sup>Department of Materials Science and Engineering, Department of Mechanical Engineering, Department of Bioengineering, and The Alan G. MacDiarmid Nanotech Institute, The University of Texas at Dallas, 800 W. Campbell Road, Richardson, Texas 75080, U.S.A.

\*E-mail: cary.baur@utdallas.edu.

This chapter provides an overview of piezoelectric vibrational energy harvesting and outlines significant advances in polymer composites for harvesting applications. The piezoelectric phenomenon is described and relevant equations are provided and explained. Several prominent types of piezoelectric materials are discussed, followed by a description of the advances made through the combination of polymers and particles to create piezoelectric composites. An in-depth description detailing how to significantly increase the piezoelectricity of poly(vinylidene difluoride) through the incorporation of carbon nanomaterials such as single-walled nanotubes (SWNTs) and Buckminsterfullerenes (C<sub>60</sub>) is given, followed by the description of a new, lead-free ceramic material that is a promising candidate for use in non-toxic polymer composites. Finally, a comprehensive description of the design and modeling of piezoelectric polymer composite bimorphs for vibrational energy harvesting is provided.

## An Introduction to Piezoelectric Energy Harvesting

The ever decreasing size and energy consumption of small electronics has driven recent efforts to enable “self-powered” devices that require no external power for operation, either continuous or punctuated. The ability to power small devices through ambient, harness-able energy is leading to a paradigm shift in modern wireless communication in which many objects around us, such as sensors and transmitters, can remain in constant communication (1). Termed the “Internet of Things”, these wireless networks work collectively to both monitor and perform designated tasks with no battery replacement or recharging and are enabled by persistent sensor nodes and underlying harvesting technologies (2). These advances have led to a growing body of research in the field of vibrational energy harvesting to enable the powering of systems through environmental vibrations. Vibration-harvesting solutions continue to be improved with new materials and composites and optimized through clever engineering solutions. Concurrently, low power electronics researchers continue to reduce power consumption and energy demands for increasingly complex sensors and sensing systems, leading to a convergence which will yield new paradigms for information exchange that will permeate many facets of life in society. Today’s bottlenecks in interacting with smart devices, such as frequent replacement of batteries or charging limited to discrete locations will be eliminated.

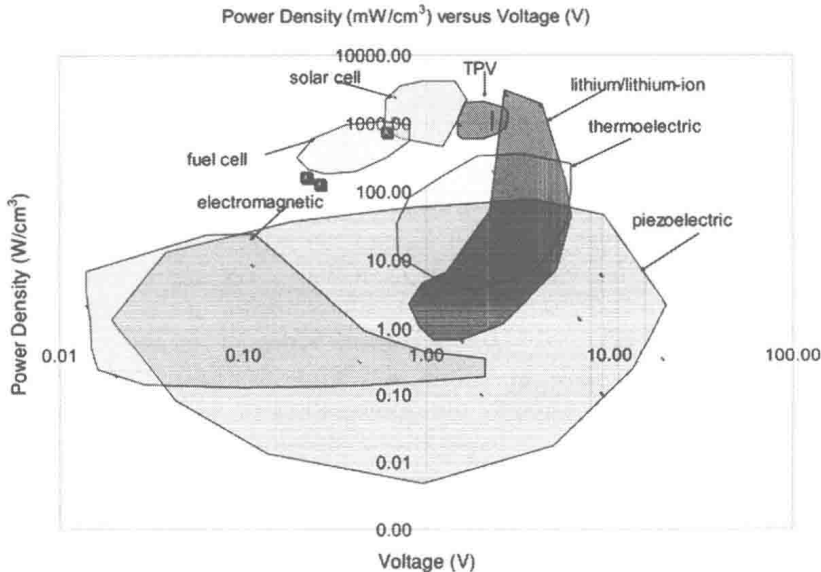


Figure 1. Power Density vs. Voltage Plot of Various Regenerative Power Supplies. Reproduced with permission from (6), 2008, © IOP Publishing.

There are three well known vibrational-to-electrical energy transduction mechanisms: electromagnetic, electrostatic, and piezoelectric (3). While all three mechanisms have been extensively explored over the last decade,

several prominent review articles have placed emphasis on piezoelectric energy harvesting due to its large power densities and ease of application (4, 5). The power density vs. voltage plot (Figure 1) shows that piezoelectric materials cover the largest range of power densities, comparable to those of lithium ion batteries and thermoelectric generators (6). In addition, while most energy harvesting mechanisms yield very low voltages that require processing and up-converting to produce a usable voltage, piezoelectric harvesters can create voltages large enough to be used directly.

While it should be noted that the power density of a material is not sufficient to absolutely compare its effectiveness in a harvesting device without knowing the input energy, it does give a rough idea of the possibilities and limitations. It is apparent from this graph that piezoelectrics have one of the best combinations of power density and voltage potential and emerging synthetic techniques for engineering polymeric piezoelectric composites hold tremendous promise for solution processable harvesting solutions with sufficient properties.

Piezoelectric materials have non-centrosymmetric point groups resulting in net distortion from their equilibrium positions with the application of an electric field or mechanical stress. This property allows for the conversion of mechanical stress into electrical charge, known as the “direct” effect, and the conversion of electrical fields to mechanical strain, the “converse” effect (7–9). Pressure sensors, structural measurement and vibrational energy-scavenging devices utilize the direct piezoelectric effect, while the converse piezoelectric effect enables shape control, active vibrational dampening, and actuation (10–13). The two most common piezoelectric parameters are the piezoelectric strain coefficient,  $d$ , and the piezoelectric voltage coefficient,  $g$ . The  $d$  and  $g$  coefficients are tensors of rank 3 defined as follows:

$$d_{ij} = \frac{dP_i}{d\sigma_j} \quad \text{and} \quad g_{ij} = \frac{dE_i}{d\sigma_j} \quad (1)$$

$$i = 1, 2, 3 \quad \text{and} \quad j = 1, 2, 3, 4, 5, 6$$

where  $P_i$  is the polarization vector,  $E_i$  is the electric field vector, and  $\sigma_j$  is the stress tensor. The two scripts  $i$  and  $j$  represent the relative directions of the values. In practical terms, the  $d_{33}$  coefficient is used to denote the induced polarization (parallel to the direction in which the material is polarized) per unit stress, or the induced strain per electric field and is typically measured in pico coulombs per Newton. The  $g_{33}$  coefficient denotes the induced electric field (parallel to the direction in which the material is polarized) per unit stress, or the induced strain per electric displacement and is typically expressed in millivolt meters per Newton

Further,  $d_{ij}$  and  $g_{ij}$  can be related by:

$$g_{ij} = \frac{d_{ij}}{\epsilon_0 \epsilon_r} \quad (2)$$

where  $\epsilon_0$  is the permittivity of free space typically measured in Farads per meter and  $\epsilon_r$  is the relative dielectric constant, a dimensionless number. From this relationship it can be observed that piezoelectric materials with high dielectric

constants generally have high  $d$  values and materials with low dielectric constants have high  $g$  values. For energy harvesting applications large  $d$  and  $g$  values are required along with material compliance and flexibility.

While the  $d$  and  $g$  coefficients provide insight into the generated charge per unit applied force, the total efficiency of energy conversion, known as the electro-mechanical coupling factor,  $k$ , can be expressed between 0 and 1 as (14):

$$k_{ij} = \frac{d_{ij}}{\sqrt{\epsilon_0 \epsilon_r s_{ij}}} \quad (3)$$

where  $s_{ij}$  is the compliance (or inverse of stiffness) typically measured in meters per Newton (15). This relationship is somewhat intuitive in that one would expect a stiffer material to experience larger internal strains, resulting in a larger internal energy. Likewise, while increasing the dielectric constant allows for a greater amount of internal charge generation, it also increases the capacitance and the force needed to displace charge, resulting in a lower efficiency.

**Table 1. Piezoelectric and Dielectric Constants of Common Piezoelectric Material\***

<i>Material</i>	<i>Relative Dielectric Constant, <math>\epsilon_r</math></i>	<i>Piezoelectric Charge Constant, <math>d_{33}</math> (pC/N)</i>	<i>Piezoelectric Voltage Constant, <math>g_{33}</math> (<math>10^{-3}</math> V m/N)</i>
BaTiO <sub>3</sub>	1700	191	12.6
Quartz	4.5	2.3 (d 11)	50.0
PVDF	13	-33	-339.0
PZT-4	1300	289	25.1

\* Reproduced with permission from ((16)), 2008, © Springer.

While the piezoelectric effect can be found in materials such as quartz, ceramics, and polymers, most piezoelectric based energy harvesting applications utilize ceramics due to their high  $d$  values. As shown in Table 1, ceramic materials such as barium titanate (BaTiO<sub>3</sub>) and lead zirconate titanate (PZT) have piezoelectric charge constant ( $d_{33}$ ) values in the hundreds of pico coulombs per Newton, while the best performing polymer, poly(vinylidene difluoride) (PVDF), possesses a much lower constant of 33 (16). Practically speaking, this renders ceramics much more suitable than polymers for strain dependent applications such as actuators. However, PVDF possesses a large  $g_{33}$  voltage constant due to its relatively low dielectric constant, making it a much more sensitive material than ceramics, requiring little force to trigger a piezoelectric response. Because of this property, PVDF is used largely in pressure and acoustic sensors.

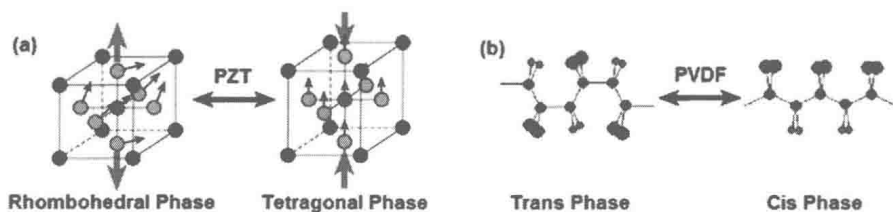


Figure 2. The non-piezoelectric (left) and piezoelectric (right) structures of (a) lead zirconate titanate (PZT) – blue atoms are Pb, green atoms are O, orange atoms are either Zr or Ti and (b) PVDF – black atoms are C, blue atoms are F, and green atoms are H. Reproduced with permission from (17), 2010, © Royal Society of Chemistry.

PZT (Figure 2(a)) possesses a rhombohedral structure at high temperatures, but upon cooling to below the Curie temperature, the unit cell conforms to a tetragonal phase, with the center zirconium or titanium atom displaced out of the geometric center, giving rise to a permanent charge displacement and piezoelectricity (17). While relatively high  $d_{33}$  constants allow ceramics to produce large voltages sufficient to charge a battery, they are naturally limited by their high stiffness, brittleness, and low processability. For many growing, high-value applications, compliant materials with lower mechanical impedance, cost and driving voltages are required (18).

The discovery of piezoelectric polymers has led to a relatively new class of elastically compliant electroactive materials (19–21). Piezoelectric polymers have been incorporated into a broad range of applications including sensors, actuators, ultrasonic imaging, integrated microelectromechanical systems and ferroelectric memory devices (22). PVDF, shown in Figure 2(b), naturally occurs largely in the non-piezoelectric *trans* phase. Through processing techniques such as thermal treatment and drawing under specific conditions, the polymer can be transformed into the piezoelectric *cis* phase in which permanent fluorine-carbon dipoles are developed. However, the low voltage and force generation of piezoelectric polymers have greatly limited their application (23). In order to enhance the performance of piezoelectric polymers, composites incorporating ceramic particles, inorganics and carbon nanomaterial have been fabricated to increase strength, stiffness, dielectric constant and piezoelectricity.

The majority of piezoelectric harvesting devices are comprised of bimorph (two layers) cantilever beams that are mounted directly to the source of vibration. Local vibration causes the cantilever to oscillate, resulting in charge movement and the production of an alternating current (24). Figure 3(left) shows a schematic representation of a typical energy harvesting bimorph. The harvester shown is composed of two piezoelectric strips that sandwich an electrode of varying thickness and stiffness, depending on the desired vibrational frequency. The outer surfaces of the bimorph are electroded with a compliant conductive metal (copper, gold etc.). The piezoelectric elements are usually electrically poled in opposite directions, thus resulting in complimentary strains with an applied voltage.



Bimorphs can be configured in either antiparallel or parallel configurations. While antiparallel actuators have only outer electrodes of applied opposite voltage, parallel systems have an inner electrode that is of opposite voltage as both of the outer electrodes (25).

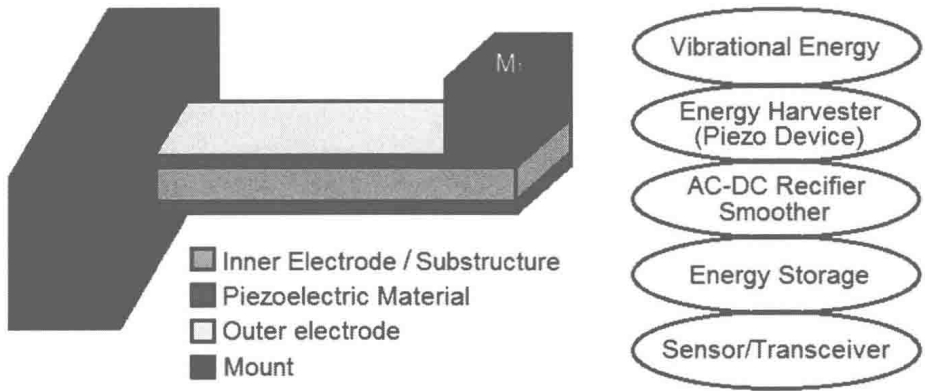


Figure 3. Piezoelectric Bimorph (Left) Piezoelectric Energy Harvesting System (Right).

A general energy harvesting circuit is described in Figure 3(right). The energy generation from the bimorph strip is in the form of an alternating current, thus resulting in a signal that must be converted into a DC voltage via a voltage rectifier in order to charge a capacitor or battery. The rectified DC voltage is often run through a smoothing capacitor or impedance controller to optimize power transfer to the energy storage unit. Finally, the harvested energy is used to power a small electronic device such as a sensor or transceiver.

### Significant Advances in Piezoelectric Polymer/Ceramic Composites

In order to overcome the low compliance of ceramics and the low piezoelectricity of polymers, Newnham and other researches at Pennsylvania State University introduced piezoelectric composites which combined passive polymer matrixes with piezoelectric ceramic particles, utilizing the distinct advantages of each material (26–29). In their work, they identified a distinction in properties between particle connectivity patterns in composites, and introduced nomenclature to differentiate these composites. The composites are annotated in the format of  $x$ - $y$ , where  $x$  is the number of dimensions in which the particles are continuously connected to each other, and  $y$  is the number of dimension in which the matrix is connected to itself. For example, a randomly oriented composite in which the particles are not connected in a defined pattern would be denoted 0-3, whereas a pillar type composite would be denoted 1-3. Polymer-ceramic composites with 0-1 connectivity have been widely researched in the past to improve flexibility, dielectric performance and piezoelectricity.