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Flexible ceramic-elastomer composite piezoelectric energy harvester fabricated by additive manufacturing

Jae-Il Park¹, Gil-Yong Lee², Jinkyu Yang², Chung-Soo Kim¹,³ and Sung-Hoon Ahn¹,³

Abstract
As a renewable energy harvesting method, interest in piezoelectric energy harvesting has increased significantly. Despite the piezoelectric energy-harvesting technology expanding its area to the flexible (elastic, amendable) energy harvesting, striking use or application of the technology is hardly found in the market. Here, we report a novel flexible piezoelectric energy harvester fabricated by using an additive manufacturing process, which enables both effective and customized manufacturing of energy harvesting devices. By advantages of additive manufacturing, further application of the piezoelectric energy-harvesting technology is highly expected. Particles of BaTiO₃, a ceramic with a large piezoelectric constant, were mixed with polyether block amide elastomer to form a flexible piezoelectric composite. The energy harvester was fabricated using an additive manufacturing process, by printing the piezoelectric composite on a laser-patterned flexible Indium-tin-oxide–coated polyethylene terephthalate substrate. Performance of fabricated energy harvester was evaluated by applying a mechanical stress to the energy harvester; voltage and current output were 2 V and 40 nA, respectively. An analytical model of the piezoelectric energy harvester was developed and discussed to explain the form of the voltage waveforms in response to the applied stress.

Keywords
Flexible piezoelectric energy harvesting, additive manufacturing, barium titanate, polyether block amide

Introduction
Various renewable energy-harvesting methods have been proposed as alternatives to fossil fuels, including driving turbines using hydropower¹² or wind power,³⁴ converting chemical energy from ‘green fuels’ to electrical energy,⁵⁶ and solar energy.⁷–⁹ Energy harvesting using piezoelectric materials can convert mechanical energy directly into electrical energy. By its simple principle of harvesting energy, piezoelectric energy harvesting is easily applicable in numerous fields where mechanical energy exists.

Recently, interest in flexible (elastic, amendable) piezoelectric energy harvester has been increased globally. A flexible piezoelectric energy harvester may be used to increase the number of applications of piezoelectric energy harvesting, due to its potential advantage of easy integration to the personalized devices. Numerous fabrication methods have been employed to achieve this.¹⁰–¹⁸ Swallow et al.¹¹ embedded lead zirconium titanate (PZT) fibers in a polymer matrix placed on metal electrodes; Kim et al.¹² synthesized ZnO nanorods on a paper-based substrate;¹² and Park et al.¹³ spin-coated a BaTiO₃/carbon nanotube/reduced graphene oxide/PDMS composite material onto a flexible substrate to create a deformable piezoelectric film.

Despite the progress of piezoelectric energy harvesting technology, there has not been a prominent application or market growth offered through the
technology. To open up the new stage of piezoelectric energy harvesting technology, there is a need to develop a piezoelectric energy harvester fabricated by the manufacturing technique which enables proper customization of piezoelectric energy harvesters to various fields.

Here, we describe a flexible piezoelectric energy harvester fabricated by novel and simple method using a nanocomposite deposition system (NCDS), which is an additive manufacturing processes involving fused deposition methods. NCDS is a technology that enables free-form objects of polymer and polymer-based composite to be fabricated without sub-processes. As additive manufacturing has significant advantages in terms of a rapid design-to-production times and customization, NCDS provides rapid fabrication of customized piezoelectric energy harvester by printing piezoelectric composite material.

In the presented research, flexible piezoelectric energy harvester was fabricated by printing a flexible piezoelectric composite material on a flexible polymer substrate using NCDS. To form a piezoelectric composite material, BaTiO₃ particles were mixed with polyether block amide (PEBA). BaTiO₃ is a ceramic material which is easily found as particle with a high piezoelectric constant, and PEBA is an elastomer with a low-density, high-mechanical strength, high-elasticity, and high-adhesive characteristics on any surface when it is heated. Due to those properties of BaTiO₃ and PEBA, piezoelectric composite with high piezoelectric and mechanical performance could easily be formed by a simple method of blending BaTiO₃ particle in molten PEBA. Also, the composite can be formed in low temperature and the melting and hardening processes of the BaTiO₃-PEBA composite is compatible with substrate materials including polymer because of the low melting point of PEBA (≈135°C). The piezoelectric composite was directly printed using NCDS on a flexible polymer substrate, to form the desired structure. Performance of fabricated piezoelectric energy harvester was evaluated by measuring the output voltage and current, and a simple model of the energy harvester was developed and discussed.

Fabrication of the flexible piezoelectric energy harvester

Figure 1 presents schematic diagram of the fabrication procedure. The BaTiO₃-PEBA composite was prepared using a simple mixing method. BaTiO₃ particles (<3 μm, Sigma-Aldrich) were dispersed in molten PEBA (Pebax®, Arkema) using mechanical stirring at 140°C. Indium-tin-oxide (ITO)-coated polyethylene terephthalate (PET) was used as the flexible substrate. Two electrodes were fabricated on the one side of the substrate to fabricate energy harvester by one step of printing process of PEBA-BaTiO₃ composite. To lengthen the length of the electrodes, interdigitated electrodes were devised. Fabrication of the electrodes was carried out using a direct writing process, whereby subtractive laser patterning of the ITO layer was involved using a CO₂ laser cutter in a 12 mm × 30 mm area. Since the area in which two electrodes should be placed was limited, interdigitated configuration could provide longer electrodes which can lead better output performance of the energy harvester. The length of interdigitated electrode was 12 mm, and the width of each finger of the electrode was about 600 μm. The milling width of laser, which defined the gap between the electrodes, was 300 μm.

A 300-μm-thick layer of the BaTiO₃-PEBA composite was deposited on the substrate using NCDS. Figure 2(a) presents the NCDS and Figure 2(b) illustrates the principle of composite deposition by NCDS. The BaTiO₃-PEBA composite was a dense liquid, melted using heat applied at the barrel and nozzle, as shown in Figure 2(b). After the composite had melted, compressed air was applied to the nozzle to form a liquid-state composite, which could be squeezed out. The composite was then deposited on the substrate and hardened into a solid state by allowing it to cool to room temperature. During deposition of the composite, a three-axis stage translated the substrate to fabricate desired features. Three different compositions of
BaTiO$_3$-PEBA composite were used: BaTiO$_3$ wt 5%, 10%, and 15%. The nozzle diameter was 500 μm, the temperature was 150°C, and the pressure of the compressed air was 50 kPa.

Finally, the structure was poled using an external electric field to align polarization of the BaTiO$_3$ particles. An electric field of 4 kV/cm was applied for 10 hours at 120°C, which is the Curie point of BaTiO$_3$. Figure 3(a) shows the interdigitated electrodes patterned on the substrate and Figure 3(b) shows the BaTiO$_3$-PEBA composite material deposited on the patterned ITO/PET film. Figure 3(c) presents a cross-sectional view of the structure.

**Experiments and results**

The flexible piezoelectric energy harvester was analyzed by measuring the output voltage and current in response to a force of 20 N with 0.5 m/s$^2$ of acceleration applied over the 12 mm × 20 mm area of the device using a one-axis translation stage to deform the structure. Kistler Type 9265C dynamometer (Kistler, USA) was used to measure applied force. Electrical measurements were performed using a Keithley 6514 electrometer (Keithley, USA).

Figure 5(a) shows the measured open-circuit voltage in response to deformation, and Figure 5(b) shows the short-circuit current. Both the voltage and current exhibited positive and negative peaks induced by the repetitive mechanical stressing of the piezoelectric energy harvester. Positive peaks were generated when the stress was applied and negative peaks were generated when the stress was released. Actual energy harvesting was carried out to confirm energy generation by applying force to energy harvester. By human foot stepping, ~600 N of force was applied on the energy harvester.
harvester for 20 minutes (~1000 times). Generated energy was captured in a capacitor using rectifier circuit system which is presented in Figure 5(c), and powered LED successfully for ~0.5 second.

Figure 6(a) and (b) compare the voltage and current between structures formed with different fractions of BaTiO3, presented as the half of peak-to-peak value in a single stressing cycle. Voltage and current increased as BaTiO3 content increased: with a BaTiO3 content of wt 15%, the average peak voltage was 2 V and the average peak current was 40 nA; the maximum peak values observed were 3 V and 50 nA. The peak power and RMS power of the energy harvester were 0.072 mW (0.030 mW per cm2) and 0.008 mW (0.003 mW per cm2), respectively.

Error bars in Figures 6(a) and (b) indicate irregularity of output voltage and current. Irregular magnitude of the output signals might be occurred by some reasons. BaTiO3 particle could not be distributed perfectly in the PEBA matrix and the force impacts on the energy harvester were not perfectly same every time. Also, there were some outliers in signals generated by measurement errors of electrometer. Since we used data with no artificial processing, outliers which were supposed to be measurement failures in the data made the error bars larger.

Discussion

Figure 7 presents a magnified voltage trace during single impact based on the data shown in Figure 5. During the rising part of the peak, the potential difference results from the piezoelectric effect of the BaTiO3 particles in the composite when the stress was applied. This causes a current to flow in the circuit of the piezoelectric energy harvester and the measurement system, which in turn causes the voltage to drop, resulting in the decaying part of the curve, as shown in Figure 7.
The potential difference is induced between electrodes by the piezoelectric effect in response to an applied mechanical stress, which defines the amplitude of the peak. Then, the current induced by piezoelectric voltage can be described by the equivalent circuit shown in Figure 8(a). The voltage between the electrodes can be derived by applying Kirchhoff’s circuit laws

\[ V - \frac{Q_g}{C_g} - iR_g - iR_L = 0, \quad (1) \]

where \( Q_g \) is the charge between the electrodes, \( C_g \) is the equivalent capacitance of the energy harvester, \( R_g \) is the equivalent resistance of the energy harvester, and \( R_L \) is the resistance of the load, i.e. the measurement system.

Then the voltage applied to the load, \( V_L \), can be expressed as

\[ V_L = \frac{R_L}{R_g + R_L} V e^{-\frac{t}{R_g C_g}}, \quad (2) \]

The decaying part of the voltage peak was mathematically compared with the calculated form in equation (2). The data fit well to an exponential decay model, as shown by the regression curve in Figure 8(b), where the coefficient of determination was \( R^2 = 0.99554 \).

![Figure 6. Comparison of the half of peak-to-peak (a) voltage and (b) current in the piezoelectric energy harvesters with different BaTiO\(_3\) contents.](image)

Applying this model, the electric energy produced by piezoelectric energy harvester during a single voltage peak can be calculated by integrating the power consumption. By ignoring the rise time, the electric energy in a single peak can be expressed as

\[ W \sim \frac{1}{2} C_g V^2 \frac{R_L}{R_g + R_L}. \quad (3) \]

From the above equation, the electric energy generated increases as \( C_g \) or \( V \) increases, or as \( R_g \) decreases. In other words, a short distance between the electrodes, high BaTiO\(_3\) content, or a low resistivity should improve the efficiency of the piezoelectric energy harvester. However, it is not always possible to control these three parameters independently, and furthermore, we are constrained by the manufacturing processes.

In particular, a large BaTiO\(_3\) content increases the chances of structural problems with the fused-deposition-based additive manufacturing process, as it may interrupt the flow of molten composite. Additionally, it may reduce the mechanical strength and elasticity of the composite. ITO was used for electrode material on flexible PET substrate in this work. As the printing process of the BaTiO\(_3\)-PEBA composite is compatible on various substrate materials including polymer, electrode and substrate material with higher conductivity can be selected depending on use, which can lead to improvement of internal resistance \( R_g \). In future work, the parameters should be analyzed further to find optimized conditions for fabrication, and thereby enhance the performance of the flexible piezoelectric energy harvester.

**Conclusions**

A flexible piezoelectric energy harvester was successfully fabricated by novel and simple method by applying an additive manufacturing process. A piezoelectric
composite was fabricated easily by dispersing piezoelectric BaTiO₃ ceramic particles into a PEBA elastomer matrix in heating condition at low temperature. Then flexible piezoelectric energy harvester was fabricated using NCDS, by printing BaTiO₃-PEBA composite on a flexible polymer substrate. The flexible piezoelectric energy harvester showed reasonable performance for potential use as an actual energy harvesting device by measuring the output voltage and current, which had amplitudes of 2 V, 40 nA when a stress was applied. An analytical model was developed to describe the piezoelectric energy harvester, and the measured data were described using regression to the analytical expressions.

Presented method using additive manufacturing can provide very short design-to-production time and production of complex, customized structures including 2.5D and 3D structures potentially. Also, excellent mechanical stability is expected compared to previous flexible energy harvesters due to outstanding mechanical properties of PEBA. By its advantages of easy fabrication and customization, the energy harvester introduced in this work can realize actual application on various fields including personalized device. Also, it showed possibility of application by actual energy harvesting. Further improvement of the performance of the energy harvester is expected by carrying out parametric study to find optimized parameter sets including the material properties of the BaTiO₃-PEBA composite and electrode configurations.

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Conflict of interest
None declared.

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