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Energy Conversion Model and Extrusion 3D Pringting of Piezoelectric Composite Energy Harvesters

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***Abstract*—Piezoelectric energy harvesters can realize conversion from mechanical energy to electric energy and power the electronic devices. In this work, based on the electro-elastic model of piezoelectric composites, considering the influence of external load on the piezoelectric coupling, a mathematical model for calculating the energy output of the piezoelectric energy harvesters is established through the coupled equations of elastic and electric fields, Kirchhoff's Circuit Law and the law of charge conservation. Barium Titanate/polydimethylsiloxane (BTO/PDMS) composites were fabricated by extrusion 3D printing. In addition to the conventional extrusion in air, a new water bath extrusion approach was also used to prove its feasibility in preparing piezoelectric composites. The results show that water bath extrusion has advantages in maintaining the shape of the structure. Moreover, the piezoelectric properties were evaluated by falling ball impact tests. The peak-to-peak value of the pulse produced by the energy harvester extruded in air and water bath were 1.74 V and 3.31V, respectively. The energy harvesters extruded in water bath achieved 1.9 times of output voltage of that extruded in air.**

Keywords- piezoelectric composite energy harvester; mathematical model; extrusion 3D printing; water bath

I. INTRODUCTION

The application of wearable flexible electronic devices requires a large number of portable or wearable power supply. As a promising technology, flexible energy harvesters have received extensive attention due to their ability to harvest and utilize energy from the environment to power electronic devices [1], [2]. Due to the special crystal structure of piezoelectric material, charges will be generated on the surface when external stress was applied. The energy conversion can be realized by energy harvesters through piezoelectric behavior [3]. Among piezoelectric materials, although lead-containing ceramics have better energy conversion performance, lead is biologically toxic and not suitable for wearable devices. Lead-free Barium Titanate (BTO) has become one of the research hotspots. BTO ceramic has good energy conversion effect with piezoelectric coefficient d_{33} 190 pC/N [4]. Piezoelectric ceramics are brittle and not applicable in wearable devices directly. Therefore, scholars disperse ceramic ceramics in a polymer matrix and package it to improve the ductility and enable materials to work at a large strain [5]. Polydimethylsiloxane (PDMS) is chemically stable and easy to form, so it is one of the most popular matrix materials [6].

The properties of piezoelectric materials will affect the energy conversion performance of harvesters, and composite properties has been extensively studied. Krishnaswamy et al. [7] calculated the effective piezoelectric coefficients by electro-elastic model to evaluate the performance of piezoelectric composites with different structures and matrix materials, which can be used for composite design. Nafaria and Sodano [8] also studied the properties of composite materials with different structures. Mori-Tanaka model and finite element method (FEM) were used to calculate the piezoelectric coefficients and the results were verified by experiments. Although above models can accurately evaluate the performance of piezoelectric composites, the influence of external load on electric potential is not considered. It is well known that the properties of piezoelectric materials are not equivalent to those of energy harvesters. When the energy harvester is connected to a circuit, electric charges are generated on the surface of the piezoelectric material under the applied pressure, and a current is formed, which in turn generates an electromotive force through the load. Since the load and the piezoelectric material are in the same circuit, the electromotive force of the load will also affect the potential on the surface of the piezoelectric material, thereby affecting the electric field distribution inside the material.

There are many fabrication methods for piezoelectric composite energy harvesters. Yang et al. [9] prepared Barium Titanate/polyvinylidene fluoride (BTO/PVDF) composites by casting, and the output voltage was 9.3 V under the 12 N force compression. Gao et al. [10] prepared BTO micro-platelets/PDMS composites by spin coating. The maximum output voltage and current of energy harvesters are 6.5 V and 140 nA by motor bending. Materials extrusion 3D printing technologies can also be used to fabricate piezoelectric composites by depositing the material through a nozzle to make the desired structure. The extrusion materials called ink should have shear thinning behavior, which is conducive to be extruded and keep shape after extrusion [11]. Piezoelectric composites fabricated by extrusion 3D printing are formed layer-by-layer, which reduces the material agglomeration during curing compared to the casting method. Material distribution can also be controlled by this method. Kim et al. [12] compared the BTO/PVDF film prepared by fused deposition modeling extrusion 3D printing and solvent casting. It was found that higher degree of agglomeration, porosities, and cracks would appear on the bottom surface of cast films. However, due to the fluidity of printing materials, extrusion 3D printing has the disadvantage of low printing resolution. The low viscosity of BTO/PDMS materials results in significant material flow during printing and curing, resulting in poor fabrication quality [13]. In order to improve the printing resolution, scholars have proposed a method by immersing the printing substrate and the nozzle in distilled water, which can utilize the pressure of the water to restrict the flow and deformation of the material. This method is helpful to improve the printing quality, but it has not been applied to the preparation of piezoelectric composites for flexible energy harvesters.

In this work, on the basis of electro-elastic model, the influence of external load on the piezoelectric coupling and the electric field distribution of piezoelectric materials is considered, and combining Kirchhoff's Circuit Law and the law of charge conservation, a mathematical model is established to calculate the energy output of piezoelectric energy harvesters. The energy harvesters are fabricated by above-mentioned extrusion 3D printing technologies. The feasibility of the water bath extrusion is verified, and the piezoelectric properties of energy harvesters prepared by conventional extrusion and water bath extrusion are compared and analyzed.

II. ENERGY CONVERSION MODEL OF ENERGY HARVESTERS

Piezoelectric energy harvesters can converse the mechanical energy into electrical energy for power supply of electronic devices. This process is shown in Fig. 1. When the piezoelectric material is connected to the circuit, under the action of alternating pressure, the alternating charges formed on the surfaces of the piezoelectric material will generate a current through the outer loop, thereby powering to load.

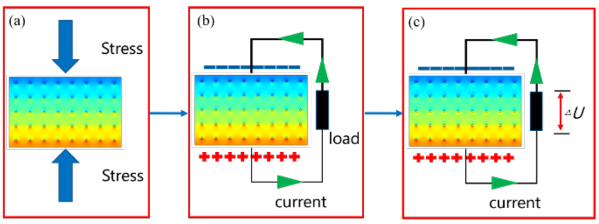

Figure 1 The schematic diagram on how energy harvester to power devices

The amount of piezoelectric charges generated is affected by the stress field, the electric field and the coupling of the two, and the physical law of them can be expressed by (1)-(6). The mechanical behavior of composite materials satisfies Newton's Second Law, and the electrical behavior satisfies Gauss's theorem, which can be described using (1)-(2), as follows [7], [14]:

$$T_{\mathrm{ij,i}} + f_{\mathrm{j}} = \rho \ddot{u}_{\mathrm{j}} \quad (1)$$

$$D_{\mathrm{i,i}} = \rho_{\mathrm{f}} \quad (2)$$

where, T_{ij}, f_j, ρ and u_j are the stress tensor, body force, material density and displacement,respectively. And D_i and ρ_f refer to electric displacement vector and body charge density.

The relationship between strain and displacement, and that between the electric field and electric potential are described as follows:

$$S_{\mathrm{ij}} = \frac{1}{2}\left(u_{\mathrm{i,j}} + u_{\mathrm{j,i}}\right) \quad (3)$$

$$E_{\mathrm{i}} = -V_{,\mathrm{i}} \quad (4)$$

where, S_{ij} is strain tensor, and E_i and V respect electric field and electric potential.

The coupling relationship between strain and the electric field of piezoelectric material are [15]:

$$T_{\mathrm{ij}} = C^{\mathrm{E}}_{\mathrm{ijkl}} S_{\mathrm{kl}} - e_{\mathrm{kij}} E_{\mathrm{k}} \quad (5)$$

$$D_{\mathrm{i}} = e_{\mathrm{ikl}} S_{\mathrm{kl}} + \varepsilon_{\mathrm{ik}} E_{\mathrm{k}} \quad (6)$$

where, C_{ijkl}, e_{ijk} and ε_{ik} are elastic, piezoelectric and dielectric constant tensors, respectively.

As shown in Fig. 1(b), the load and the piezoelectric material are in the same loop. When the current passes through the load, an electromotive force will be formed, which will inevitably affect the potential on the surface of the piezoelectric material and even the electric field distribution inside the material. Thus, additional governing equations need to be added to consider the influence of load's electromotive force.

When the resistance value of the external load is R, the connection point between the electrode and the conductor is taken as the node to establish Kirchhoff's First Law, and the Kirchhoff's Second Law is established for the whole circuit. Combining the law of charge conservation, the following equations can be obtained:

$$I(t) = \iint_{A} J(t)\,\mathrm{d}A \quad (7)$$

$$I(t)R = V \quad (8)$$

$$\nabla \cdot J(t)+\frac{\partial \rho_f(t)}{\partial t}=0 \tag{9}$$

where, I is the current in circuit and J refers to current density on the electrode surface.

Overall, equations (1)-(9) show the complete physical process of the energy harvesters powering the load by physics laws. For piezoelectric composite materials, the piezoelectric constant e_{ijk} of matrix is 0 because there is no piezoelectric effect on matrix material. If the body force is not considered, f_j in equation (1) is 0.

When the external load is not pure resistance, the formula (8) can be modified according to Kirchhoff's Second Law. Mechanical boundary conditions and zero-potential points can be set according to specific application. The electrical energy utilized by load can be obtained by integrating the product of the voltage and current of the load.

III. Fabrication and Performance Test of Energy Harvesters

A. Materials

The piezoelectric material used in the experiment is BTO (99.9%, metals basis, d<100nm), purchased from Aladdin, Shanghai. Dow Sylgard PDMS 184 is used as matrix. Copper sheets with a thickness of 0.1 mm are used as the electrode. The energy harvesters are packaged by PDMS and PI films.

B. Fabrication process of BTO/PDMS films

The schematic of energy harvester structure is shown in Fig. 2. The energy conversion is realized by the piezoelectric composite material in the middle, and copper sheets are used as electrodes and they are connected to the load through conducting wire which allows for charges generated by the piezoelectric material moving. The PDMS and Polyimide (PI) film is used to package and protect the composite material.

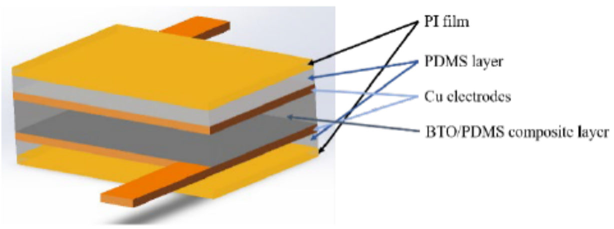

Figure 2 Schematic of energy harvester structure

For the preparation of composite materials, the printing ink is firstly configured. The PDMS was prepared by mixing ratio between the base and catalyst of 10:1, and then BTO powder is added to configure a mixed suspension with a mass fraction of 10 %. The suspension was placed in a magnetic stirrer at 2,000 rpm for 10 minutes, and then placed in a vacuum for 10 minutes to remove air bubbles from the material.

The material was transferred to the dispensing barrel, and the shear-thinned material is extruded from the nozzle by compressed air. The nozzle was placed on a three-axis moving platform, and the material can be distributed on demand through the movement of three axes. The schematic of traditional extrusion in air and water bath extrusion is shown in Fig. 3. We used the nozzle with an inner diameter of 22 G (410 μm) for extrusion, and the extrusion pressure and printing speed were determined by experiment. For the printing pressure, different pressures from small to large were applied to extrude ink until the material can flow out of the nozzle continuously and stably, and the corresponding pressure can be determined as a reasonable extrusion pressure. The printing speed is determined by single line extrusion. Different speeds were chosen to print line structure on copper. The structures were measured after printing. We chose 20 sections of printed lines for each speed and calculated the average size. The extrusion speed can be chosen according to the measurement results.

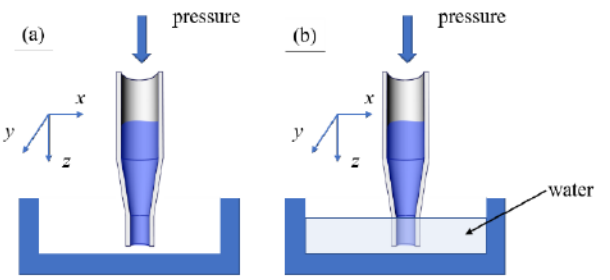

Figure 3 Schematic of traditional extrusion in air and water bath extrusion

The piezoelectric composite film of energy harvesters can be formed by printing raster pattern with appropriate line separation. The schematic diagram of the printing path is shown in Fig. 4. Under the above-determined printing conditions, the line separation d of the raster pattern is selected according to the line width of extrusion, and the printing process path can be determined.

Figure 4 Schematic of raster pattern printing path

C. Fabrication of energy harvesters and piezoelectric voltage measurement

Based on the printing parameters and printing path determined above, the energy harvesters could be fabricated. A piezoelectric composite film was prepared by extrusion on a copper sheet, and 3 layers were printed to ensure that the composite material has sufficient thickness. After printing, the composite material was placed in an oven, and after being treated at 80 °C for 1 hour, another copper sheet was placed on the top surface of the composite material as the top electrode, and then heated for 1 more hour until the material was completely cured. PDMS was set on both sides of the obtained "electrode-composite-electrode" sandwich structure and wrapped with PI film.

In order to evaluate the output of energy harvesters, falling ball impact tests were adopted. A steel ball with a mass of 32.85 g was dropped freely from a height of 300 mm and hit the energy harvester. The output voltage was measured by the oscilloscope to evaluate the energy conversion performance.

IV. RESULTS AND DISCUSSION

A. Fabrication parameters analysis

In the material extrusion 3D printing process, the inner diameter of the nozzle, extrusion pressure and printing speed directly affect the printing quality. The smaller the inner diameter of the nozzle, the higher the printing resolution. However, the nozzle with small diameter is easy to block. The 22 G nozzle is, therefore, selected in this work, which can ensure the smooth extrusion progress. In extrusion process, the extrusion pressure should be greater than the internal friction between the flow layers of ink. However, it should be noted that if the pressure is too high, more materials will be easily extruded, which is not conducive to fabrication. The choice of printing speed is also critical. If the speed is too slow, materials are easily accumulated. In return, if the speed is too fast, the material will be pulled or even broken.

For conventional extrusion process, namely extrusion pressure in air, when the pressure is less than 60 kPa, only droplets can be printed, and the extrusion process of material is discontinuous. When the pressure is less than 100 kPa, although materials can be continuously extruded, it is not uniform. When the pressure reaches 100 kPa, the extruded material is stable, so 100 kPa is selected as the extrusion pressure for conventional extrusion process. The extrusion pressure is also determined by the same method for water bath printing. Since the pressure of water is higher than that of air, the extrusion pressure used in the water bath extrusion needs to be higher than the pressure in the air. When the extrusion pressure reaches 130 kPa, the material can be extruded more stably. Therefore, 130 kPa is used in water bath extrusion.

Fig. 5 shows the line structures obtained at different speeds in extrusion process in air and water bath. The selected processing speed is in the range of 10 mm/s - 40 mm/s. Table 1 shows the average cross-sectional width of the printing structure at four extrusion speeds. It can be found that with the increase of printing speed, the resolution of lines printed in air gradually improves. For water bath extrusion, a better resolution can be obtained in a low or medium speed (10-30 mm/s). After flowable materials curing to form the solid, the difference of printed lines width through different extrusion methods will be more obvious.

Although the different of width of lines printed in different methods measured immediately after printing is not that great, as the curing time increases, the advantages of the water bath to restrict the material flow will be more obvious, and the difference in resolution between two methods will be larger after curing. It is because that the water bath can effectively restrict the material flow during curing. However, when the speed is high (40 mm/s), the printing performance will be worsened. This is due to the high-speed moving of extrusion nozzle agitates water, which can cause the instability of the system and further affect the fabrication quality of the extrusion 3D printing. In addition, during the heating and curing process, the air dissolved in the water will gather at the interface of the two materials, affecting the structure quality or even causing the failure of printing.

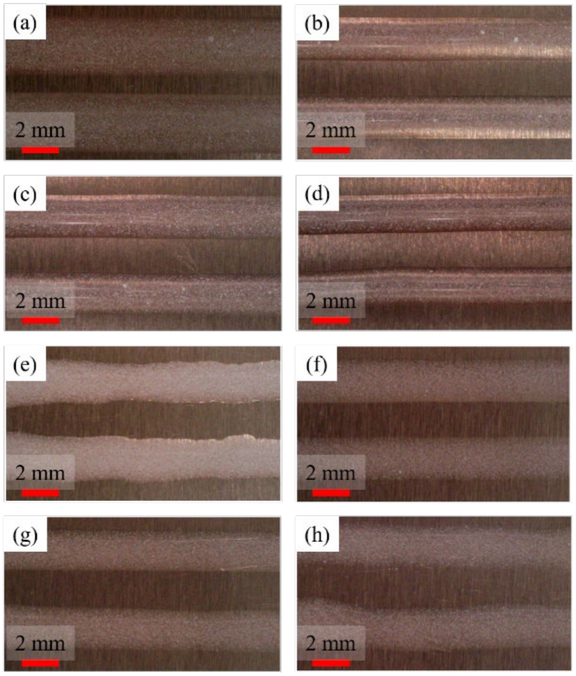

Figure 5 Line structure extrusion in air or water bath extrusion: (a)-(d) extrusion in air with speed 10 mm/s (a), 20 mm/s (b), 30 mm/s (c) and 40mm/s (d); (e)-(h) water bath extrusion with speed 10 mm/s (a), 20 mm/s (b), 30 mm/s (c) and 40mm/s (d)

TABLE I. LINE WIDTH BY DIFFERENT PRINTING METHODS AND SPEED

Printing speed	Line width printed in air (mm)	Line width printed in water (mm)
10mm/s	3.313	2.444
20mm/s	2.476	2.399
30mm/s	2.401	2.323
40mm/s	2.210	2.408

Overall, a pressure of 100 kPa is used in extrusion in air and 130 kPa is used for water bath extrusion. The same speed 30 mm/s is chosen. The experiment results show that the line width, which can also be regarded as the printing resolution, are 2.401 mm and 2.323 mm, for two extrusion methods. Therefore, when the printed line separation is 2 mm, there is no spacing between the two lines, and the film can be obtained. The overlap rate of the line extruded in the air is 20.05%, and the overlap rate of the water bath printing line is 16.15%.

B. Preparation and evaluation of energy harvesters

Using above-mentioned fabrication parameters, energy harvesters have been processed. The number of piezoelectric layers is 3, and the energy harvesters are prepared after package, as shown in Fig. 6(a). The size of the harvesters is 30 mm×20 mm. The copper electrodes were connected to the oscilloscope through wires for measuring the output voltage. Falling ball impact tests were used to evaluated the performance of energy harvesters obtained by two extrusion methods, and the generated waveform is shown in Fig. 6(b) and (c). After the ball hits the harvester, it will bounce back and hit multiple times. The figure shows the waveforms of the first 4 impacts. The voltage generated at the first impact is the largest. The maximum positive and negative pulses generated by the harvesters extruded in the air are 0.93 V and -0.81 V, respectively, and the peak-to-peak value is 1.74 V. The maximum positive and negative pulses generated by the harvester extruded in the water bath are 1.45 V and -1.86 V, respectively, and the peak-to-peak value was 3.31 V, which was 1.9 times of the harvesters extruded in air. It indicates that water bath extrusion can be used to prepare piezoelectric composite energy harvesters, and energy harvesters fabricated by water bath printing have better energy conversion performance. The possible reason for the high output voltage of the water bath extruded harvesters is good shape retention during printing and curing in bath. On the one hand, the collapse of the structure is reduced and the thickness of the harvesters is large, which is beneficial to the high output voltage, and on the other hand, the flow of the material is reduced, so that the material and the structure are more uniform.

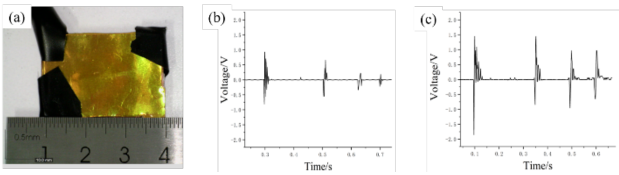

Figure 6. The energy harvester and output voltage waveform: (a) energy harvester; (b) output voltage waveform generated by harvester extrusion in air; (c) output voltage waveform generated by harvester extrusion in water bath.

V. CONCLUSION

In this work, considering the influence of external load on the piezoelectric coupling, a mathematical model for calculating the energy output of the piezoelectric energy harvesters is established based on the electro-elastic model of piezoelectric composites. The BTO/PDMS flexible energy harvesters are prepared by extrusion 3D printing technology, and their energy conversion performance of harvesters is tested and compared. The influence of water bath environment on the energy conversion performance of the energy harvesters is also analyzed. The main conclusions are as follows:

(1) For mathematical model, the influence of external load on piezoelectric coupling is analyzed. Considering the stress and electric field distribution of materials, piezoelectric coupling law, Kirchhoff's Circuit Law and the law of charge conservation, the mathematical model of energy output calculation of piezoelectric collector is established;

(2) The processing parameters are determined through extrusion experiments. The extrusion pressure used in extrusion in air is 100 kPa and the printing speed is 30 mm/s. Under this condition, the resolution of line structures printed is 2.401 mm. The extrusion pressure used in water bath extrusion is 130 kPa and the printing speed is 30 mm/s. Under this condition, the resolution of line structures printed is 2.323 mm. The structures printed in water bath environment has a higher resolution than those in air;

(3) Experiment results show that water bath extrusion can be used to prepare piezoelectric composite energy harvesters, and energy harvesters fabricated by water bath printing have a better energy conversion performance. Falling ball impact tests were adopted to evaluate the piezoelectric performance of energy harvesters. The peak-to-peak value of the pulse produced by the energy harvester extruded in air and water bath are 1.74 V and 3.31V, respectively. So the output voltage of energy harvesters extruded in water bath is as 1.9 times as that extruded in air.

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Data associated with this publication are openly available at University of Strathclyde knowledge database.

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