



Electric Poling-Assisted Additive Manufacturing Process for Lead-Free Piezoelectric Device Fabrication

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Abstract

This paper presents a new additive manufacturing method based on electric poling process often used in many polymeric materials processing for lead-free piezoelectric device fabrication. This is to directly and continuously print piezoelectric devices from Polyvinylidene fluoride (PVDF) polymeric filament rods under a strong electric field and mechanical stretching along the filament core. Piezoelectric devices were fabricated and its crystalline phase transition was measured by using the Fourier transform infrared spectroscopy. The results demonstrate that increasing the electric field increases the piezoelectric crystalline phase transitions and results in a device with higher current output under stress. This technique can be used to fabricate fully 3D freeform structured piezoelectric devices for sensing, actuator and energy harvesting applications with a simple, low cost, integrated processing and fabrication step.

Keywords: Additive manufacturing, Electric poling, Piezoelectric polymer, PVDF, Crystalline phase transition

1 Introduction

Piezoelectric materials are especially promising for a variety of devices because they can transform precise deformations over many length scales induced by small force and pressure, mechanical vibration, elongation/compression, bending or twisting into useful power or information. Such devices can be used for sensing and actuation applications as well as energy harvesting applications. Piezoelectric devices are commonly used in nearly every sector of the economy from computers, mobile, data recording, home appliance and automotive applications. However, such devices have been a concern in many commercial applications due to the potential toxic lead content. Thus, research and development of lead-free piezoelectric materials is presently one of the hottest topics in the field of piezoelectricity. There are two reasons for this interest: one is scientific (origins of the high piezoelectricity) and technological (processing, reliability), the other is related to environment and

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health. The scientific challenge is to produce lead-free systems which exhibit MPB (morphotropic phase boundary) with properties comparable to those in lead-based system. Environmental and health issues related to lead-based materials are well documented. According to RoHS, any homogeneous component containing more than 0.1 weight % of lead is subjected to restrictions; and hence, the fact that the best piezoelectric materials contain lead up to 60 weight %, may in the future, seriously hamper their use in everyday applications. This presents a significant material science challenge to create novel designs of new piezoelectric materials and how to engineer those materials to achieve similar performance to their lead-based toxic counterparts.

Table 1. Comparison of current piezoelectric polymer processing processes

Process	Stretching	Contact poling	Corona poling	Electrospinning
Poling method	▪ Mechanical	▪ Electrical	←	▪ Mechanical + Electrical
PVDF material type	▪ Sheet (cheap)	←	←	▪ Solution (expensive)
Design flexibility	▪ 1D/2D	←	←	▪ 1D
Piezoelectric performance after process	▪ Bad	←	←	▪ Good
Product types	▪ Thin-film	←	←	▪ Fiber
Productivity	▪ Slow ▪ Non-continuous ▪ Small area fabrication	←	←	▪ Slow ▪ Semi-continuous ▪ Few mm fabrication

※ ←: same as on the left

As summarized in Table 1, current PVDF processing technologies (mechanical stretching, contact poling, corona poling and electrospinning processing) cannot produce realistic piezoelectric devices with large areas of sensitivity and high degrees of alignment and uniformity in a continuous fabrication process. Realistic device functionality under small mechanical motion can be achieved with high volumetric densities. However, the state-of-art piezoelectric polymer processing can only produce 1D or 2D devices such as thin films or small diameter (millimeter scale) fibers and cover an area of only tens of cm² maximum. There are currently no known piezoelectric polymer processes possible to fabricate 3D structured piezoelectric devices with large areas of sensitivity and high degrees of alignment and uniformity. Many researchers have studied various PVDF polymer processing methods. Mahadeva created PVDF thin film using corona poling. Chang introduced lab scale piezoelectric energy harvesting devices fabricated electrospinning process. Similarly, Persano showed a high performance piezoelectric polymer fiber array sensor for bio and robotics applications fabricated by electrospinning process. Hadimani produced a continuous PVDF fiber in a melt extruder, but PVDF polymer poling direction is not along the fiber center axis, but surrounding surfaces. Egusa reported production of a multi-material fiber, which was piezoelectric. However, the multi-material and its process make the fiber expensive and difficult to scale for continuous and large area production. Moreover, the current outputs of devices produced with arrays of electrospun fiber of PVDF polymer are less than 5nA and the voltages are in the range of 1~20mV. Realistic device functionality under small mechanical motion can be achieved with high volumetric densities of aligned arrays of fibers. Current PVDF processing technologies cannot produce realistic piezoelectric devices with large areas of sensitivity and high degrees of alignment and uniformity in a continuous fabrication process. The state-of-the-art piezoelectric polymer processing can only produce thin films or millimeter scale fiber types of devices even though there is high demand in low cost 3D structured piezoelectric devices such as multi-axis dynamometers for force measurement, multi-axis actuators for nanopositioning and fiber alignment, and multi-axis energy harvester. However, there are currently no known piezoelectric polymer processing processes capable of fabricating freeform-shaped piezoelectric devices with large areas of sensitivity and high degrees of alignment and uniformity.

The research objective of this work here is to combine additive manufacturing (AM) technology with piezoelectric polymer processing technology to create a novel and transformative method to

produce lead-free piezoelectric devices capable of a few mm range of stroke and μm level positioning control for actuator applications. This technology will not only provide lead-free system exhibiting MPB with properties comparable to those in lead-based systems but also produce multilayer devices with freeform shape. We conjecture that AM and polymer processing methods can be combined to directly print piezoelectric polymers for 3D structured piezoelectric device applications. Moreover, such devices can be fabricated continuously while remaining well-aligned and uniform over a large area for sensing, actuation and energy harvesting applications. This research will produce new knowledge of combined AM and piezoelectric polymer processing. Through this new process, novel 3D structured piezoelectric devices will be tested in terms of their physical properties, performance and reliability against comparative benchmarks. The successful implementation of this research will lead to the widespread use of a new manufacturing process that can be used to make a variety of devices, with lead-free, non-toxic, ease, at low cost, in a single design, production and fabrication step.

2 Electric Poling-assisted AM Process

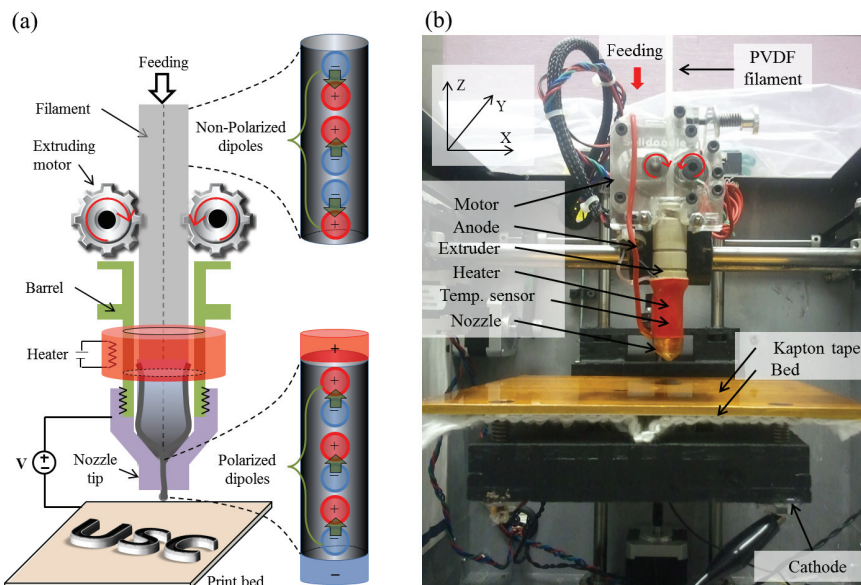


Figure 1. Piezoelectric PVDF printing system. (a) Schematic diagram of electric poling-assisted additive manufacturing (EPAM) process and (b) Experimental setup combined additive manufacturing process and electric poling process.

The electric poling-assisted additive manufacturing (EPAM) process presented in FIGURE 1(a) combines AM and electric poling processes to fabricate free-form devices continuously while maintaining uniform dipole alignment of the PVDF polymer over a large area in a single design, production and fabrication step. AM refers to a process by which digital 3D design data is used to build up a component in layers by depositing material. This technology is ideal for making prototypes during the early development phases of a product—significantly reducing the cost and time required for production development. The fused deposition modeling (FDM) process as one of AM processes was chosen for experiment. The FDM process begins with a software process that processes a stereolithography file by mathematically slicing and orienting the model for the build process.

Assuming that the PVDF polymeric filament is non-reactive and its dipoles are randomly distributed in the solid, a high electric field is applied to the molten polymer column between the nozzle tip and printing bed, which provides molecular chain alignment and transforms the polymer from an predominantly α phase crystalline structure to a β phase crystalline structure. One of the models used to explain the poling process involves rotation by 180 degree of each polymer chain along its own axis and another model involves also a rotation by 60 degrees.

Here the FDM machine (Solidoodle Corp.) was modified to be able to apply a high electric field between a nozzle tip of extruder and printing bed while printing. The PVDF polymer filament is inserted into an extruder along the feeding direction. The extruder is a stepper motor-driven filament feeding mechanism, heater, temperature sensor and nozzle tip. The PVDF polymer is heated by a heater as it is extruded by the motor through the nozzle tip with a diameter of 0.4mm as seen in FIGURE 2. Temperature is feedback controlled. High voltage is applied between the nozzle tip as an anode and the printing bed as a cathode. The printing bed is heated by an internal heater to help the molten polymer adhere to the object and avoid thermally induced cracks. Kapton tape (0.2mm thickness) on the printing bed is applied for thermal and electrical insulation. This process indicates that the semi-molten polymer column in the gap between the nozzle tip and printing bed has all the dipole moments pointing along the same biased direction and maintains polarity while printing structures. During the EPAM process, the molten PVDF polymer undergoes mechanical stress by the leading nozzle while being subjected to a strong electric field under specific high temperature as seen in FIGURE 1(a). The semi-molten polymer hardens immediately after extrusion from the nozzle. PVDF polymer experiences drawing at high temperature, electric poling at high electric field and annealing at high pressure. This unique combination of processes all contribute to the creation of the β phase crystalline structure. The processes causing crystalline phase transformation for PVDF have been well-introduced in previous studies. The printed PVDF polymer devices are expected to have a strong β phase conformation resulting from the EPAM process.

3 Results

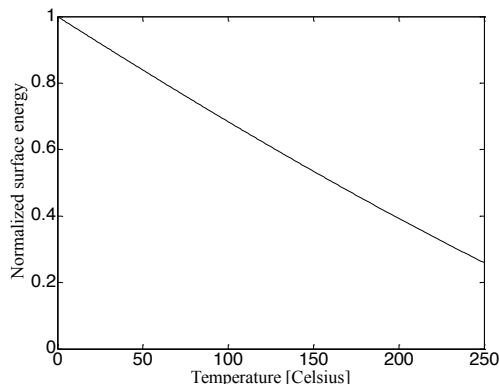


FIGURE 2. Surface energy curve of PVDF with respect to temperature.

In this research, several types of materials as a first printing layer were applied because printability is highly dependent on the surface energy of each printing layer material in contact with semi-molten PVDF polymer: Kapton tape, glass (smooth), glass (rough), Cu, and Adhesive tape. In addition, the surface energy of PVDF polymer varies with respect to temperature as shown in FIGURE 2 (Guggenheim, 1949). The experiment conditions are tabulated in TABLE 2. Highly adhesive tape was

selected and placed on the base film as a target surface for printing sample because PVDF does not adhere to the base film, Kapton tape due to the surface energy difference. The experimental conditions such as extruder feedrate, filament feedrate, extruder temperature, and bed temperature were selected to print piezoelectric devices for high printability and surface quality.

TABLE 2. Summary of printability according to printing target surface and temperature

Material		Kapton tape	Glass (smooth)	Glass (rough)	Cu	Adhesive tape
Surface energy (dynes/cm)		50	250	500	1,103	unknown
Results	Bed temp. 100°C	F	F	F	F	S
	Bed temp. 50°C	F	F	F	F	S
	Room temp.	F	F	F	F	S
Remark		1) Surface energy: PVDF 30 (dynes/cm) 2) Extruder temp. 230°C, extruder feed 200mm/min. and filament feed 30mm/min. ※ S: success and F: failure				

It can be seen that the surface energy of PVDF polymer decreases a third when temperature reaches 230°C, which is the extruding temperature. We found that the molten polymer could not stick to the target surfaces, Kapton tape, Glass and Cu, at three different printing bed temperature conditions, but it could completely stick to the adhesive tape (3M tape) at all temperature conditions. Here the bed temperature was set to 100°C for experiment, which helps the thermoplastic material adhere to the object to hold it in place and avoid thermal shocks which could cause the object to crack.

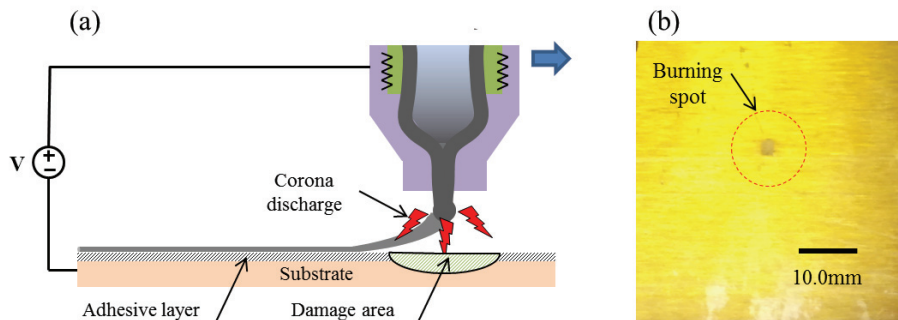


FIGURE 3. Printing surface damage due to the corona discharge

To investigate the effect on piezoelectric characteristics of the PVDF polymer with respect to the electric poling condition, PVDF polymer devices, 100mm long, were printed under four different conditions of electric field: 0.0MV/m, 1.0MV/m, 2.0MV/m and 3.0MV/m. The printing gap between the nozzle tip and printing top surface was set to 0.3mm. During poling with an electric field of 3.0MV/m electrical breakdown occurred causing burning in the first printing layer and difficulty in maintaining a constant electric field. Therefore, at 3.0MV/m it was not possible with the current setup to create a poled piezoelectric polymer which requires a static electric field (FIGURE 3). While printing, the PVDF polymer experienced mechanical stretching and electric poling simultaneously. The diameter of ten samples fabricated under extruding only and printing processes, respectively, was measured. The diameter of the PVDF polymer, $D_0 = \varnothing 0.65 \pm 0.02 \text{mm}$, was thermally-expanded as the molten polymer came out of the nozzle with a diameter of 0.4mm, and then, its diameter was shrunk to

$D_1 = 0.49 \pm 0.01 \text{ mm}$ by mechanical stretching. It was considered that the printing conditions used here can stretch the PVDF polymer 1.8 times (square of D_0/D_1) its nominal length in a uniaxial direction.

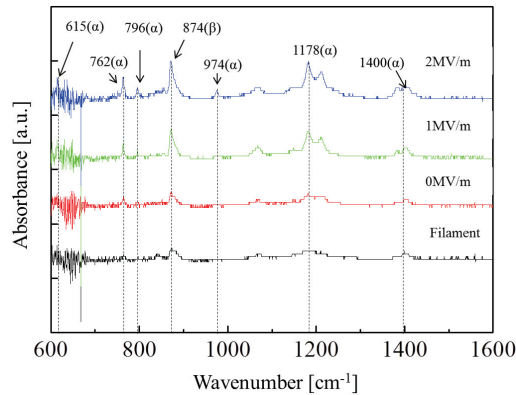


Figure 4. FTIR measurement results.

The crystalline phase of samples fabricated under three different electric poling conditions was characterized. A Fourier Transform Infrared Spectroscopy (FTIR, Galaxy series FTIR 5000) was used to obtain an infrared spectrum of absorption of each PVDF polymer sample fabricated by the EPAM process under different electric poling conditions as shown in FIGURE 4. The results indicate that samples without the electric field applied show nearly identical results with those of PVDF polymeric filament before extrusion. On the other hand, new peak, 974 cm^{-1} , was found in the samples fabricated under the strong electric field. In addition, existing peaks became sharp at certain wavenumbers, 762, 796, 874, 1178, and 1400 cm^{-1} . In the samples fabricated under a strong electric field, the peaks could be clearly seen at the wavenumber, 87 cm^{-1} , whose crystalline structure is a known β phase, and the wavenumber 1178 a known α phase. In addition, it was found that those peaks show the tendency to being sharper as the strength of electric field increases.

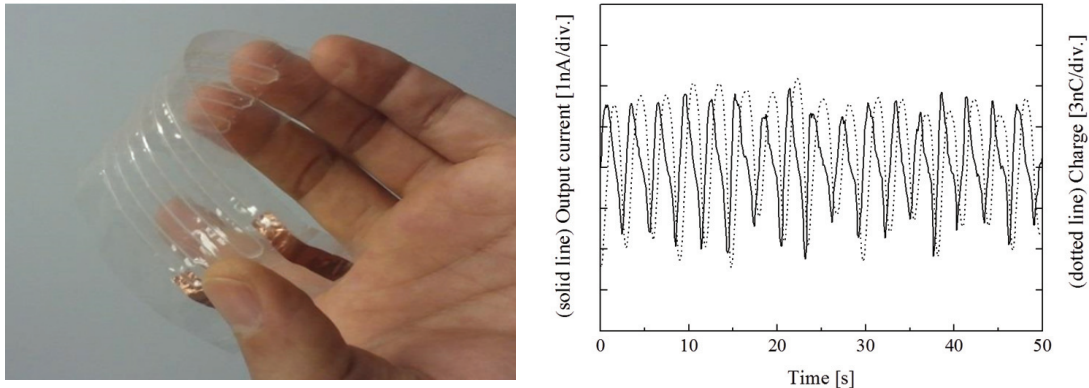


Figure 5. Fabrication of large areal and flexible piezoelectric device: (a) Image of flexible piezoelectric device fabricated by EPAM process. The electrodes, Cu, were placed at both ends of PVDF piezoelectric device. (b) Testing results: output current, $\pm 1.5 \text{ nA}$, and charge, 12.0 nC , generated when it is subjected to the cyclic bending by hand.

As a preliminary research result, complex-shaped PVDF polymer devices ($100 \text{ mm} \times 50 \text{ mm}$) were fabricated in a flexible configuration as seen in FIGURE 5(a). The PVDF polymer was printed on an

adhesive layer and Cu tape was applied on both ends as electrodes. A second adhesive layer was applied to make a laminated sample. The output current was measured while bending and releasing the device by hand. It produced approximately $\pm 1.6\text{nA}$, which was periodic with bending and uniform over 50 seconds. The total charge generated was estimated approximately as 12.0nC .

4 Conclusion

A transformative AM-based novel process was presented to fabricate freeform-shaped volumetric piezoelectric devices by combining AM and electric poling processes in a single processing and fabrication step. Piezoelectric samples were successfully printed by the EPAM process. FTIR measurements and dynamic testing showed that PVDF polymer printing without a strong electric field does not produce dipole alignment. However, devices printed under a strong electric field become piezoelectric. Stronger electric fields produce greater piezoelectricity in the devices and cause sharper peaks at the polar β crystalline wavenumber of the PVDF polymer. The results indicate that the EPAM process can provide dipole alignment of the polymer molecular chain alignment and transform the polymer from α phase to β phase by applying a strong electric field while printing simultaneously. Moreover, this process is expected to lead to the widespread use of a new manufacturing process to be able to make a variety of lead-free devices for sensing, actuation and energy harvesting and storage applications, with ease, at low cost, in a single design, production and fabrication step.

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