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ORIGINAL ARTICLE

Polyvinylidene fluoride (PVDF) direct printing for sensors and actuators

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Abstract

This paper represents a polymeric piezoelectric manufacturing process for sensing and actuation applications. The electric poling-assisted additive manufacturing (EPAM) process combining additive manufacturing (AM) with polymeric poling process has been recently introduced. This process keeps piezoelectric polymer dipoles well-aligned and uniform over a large area in a single-step direct printing process. Here, the EPAM process was employed to directly print polyvinylidene fluoride (PVDF) polymer; sensing and actuation performance was tested with dynamometer, a baseline comparison measuring instrument. Also, the plasma-assisted poling process that potentially increases piezoelectricity was briefly introduced and discussed with a preliminary result. As a result, this study promises new multi-functional materials, novel designs, and approaches in a single AM and fabrication step by combining AM with piezoelectric polymer poling methods in convenient, fast, and precise manner.

Keywords Polymeric piezoelectric · Electric poling · Additive manufacturing · Polyvinylidene fluoride (PVDF) · Sensors and actuators

1 Introduction

Currently, piezoelectric devices are used in almost every type of sensor and represent an $18BN global market with the majority of devices constructed from lead zirconium titanate (PZT) [1, 2]. Recently, concerns about lead (Pb) toxicity have caused bans on such devices; restrictions have been placed on the use of lead-based piezoelectrics from many commercial applications. Research and development of lead-free piezoelectric materials is presently a topic of great interest to sensor and actuator manufacturers currently relying on lead-based products such as the predominately used lead zirconate titanate or PZT. There are two reasons for this interest: one is scientific characteristics (origins of the high piezoelectricity, processing, reliability), the other is related to environment and health. One scientific challenge is in understanding why some lead-free systems can exhibit significantly increased piezoelectric effects on a morphotropic phase boundary (MPB) with properties comparable to those in lead-based system even though this behavior is not predictable from first principles. Environmental and health motivations for lead-free sensors are related to Pb toxicity when lead is the main constituent of most piezoelectrics [1–3]. This scientific challenge of creating new lead-free piezoelectric materials is a motivation for this study. There has been increasing interest in discovering the piezoelectric behavior of both synthetic and natural polymers as an alternative to lead-based piezoelectric materials because of the flexibility of combining structural design, ease of processing, good chemical resistance with large areas of sensitivity, simplicity in device design, and associated potential for low cost implementation.

In general, piezoelectric polarization can be produced by a two-step process of application of either tensile or shear stresses to produce thin films followed by a method to produce dipole alignment of the dielectric polymer [4]. This is currently accomplished with either high-voltage poling or corona discharge of thin films. Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer commercially available as solution, filament, powder, granules, or semi-transparent films. PVDF is also the most widely studied polymer that can exist in piezoelectric form with

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current applications in thousands of sensing [4–6] and actuation [7, 8] applications due to its low cost, chemical robustness, and favorable mechanical properties [9].

When a piezoelectric polymer is subjected to a mechanical load, positive and negative charges generate on the material surface [2]. This "smart" ability of the material allows it to convert mechanical energy into electrical energy and vice versa. Linear piezoelectric constitutive relations are derived from thermodynamic principles and couple linear elastic relations with linear dielectric relations through the piezoelectric devices. Under small field conditions, the constitutive relations for a piezoelectric material can be expressed in terms of a sensor or actuator according to the 1987 IEEE Standard. When a piezoelectric device is exposed to a stress field, it generates a charge in response, which is measured by using a charge amplifier. Actuator applications are based on the converse piezoelectric effect, the piezoelectric material is typically bonded to a structure and an external electric field is applied and a strain field is induced causing displacement as a result.

PVDF exists in α-, β-, γ-, and δ-crystalline phases depending on the chain conformation. The relative quantity of each is dependent on the thermal, mechanical, and electrical processing conditions used to produce the PVDF film or fiber [9]. The phase of PVDF is responsible for its piezoelectric properties because the piezoelectricity is based upon dipole orientation within the crystalline phase. As seen in Fig. 1, the non-polar α phase has random orientation of dipole moments while the polar β phase has all the dipole moments pointing in the same direction in all-trans zigzag conformation. The β phase is responsible for the piezoelectric property of the polymer [9, 10]. The phase of PVDF polymers is transformed by means of mechanical stretching to produce thin films with residual stresses that help maintain the β phase, contact poling, corona poling, or electrospinning process in order to provide for dipole alignment of the polymer [3]. It has also been shown that the crystalline phase transformation takes place in annealing, drawing, or poling process under a certain temperature, pressure, and electric field as seen in Fig. 2. The diagram indicates that drawing below 80 ° C, poling with a strong electric field and annealing at high pressure produce dipole alignment of dipole moments as seen in Fig. 1b. These properties are exploited during printing.

2 Piezoelectric polymer poling methods

2.1 Current piezoelectric polymer processing methods

Piezoelectric PVDF polymers are created by first mechanical stretching to produce the β phase, followed by contact poling or corona poling (or electrospinning) to produce dipole alignment of the polymer (Fig. 3) [3]. Stretching PVDF 4–5× nominal length in either a uniaxial or biaxial direction provides molecular chain alignment and transforms the polymer from its nominal α phase crystalline structure without piezoelectric properties to its β phase structure which has piezoelectric properties. Applying a strong electric field to β phase PVDF results in dipole alignment along the electric field and is referred as contact poling (Fig. 3a, b). Corona poling ionizes air molecules above the material through the use of a corona needle (Fig. 3c) which cause ions on the surface to align the dipoles due to surface charges. In order to allow the polymer chain to align and reorganize, PVDF is held at a temperature above the glass transition during poling. The current manufacturing approach of mechanical stretching, contact poling, and corona poling processes are not suitable for continuous production. Electrospinning can produce continuous

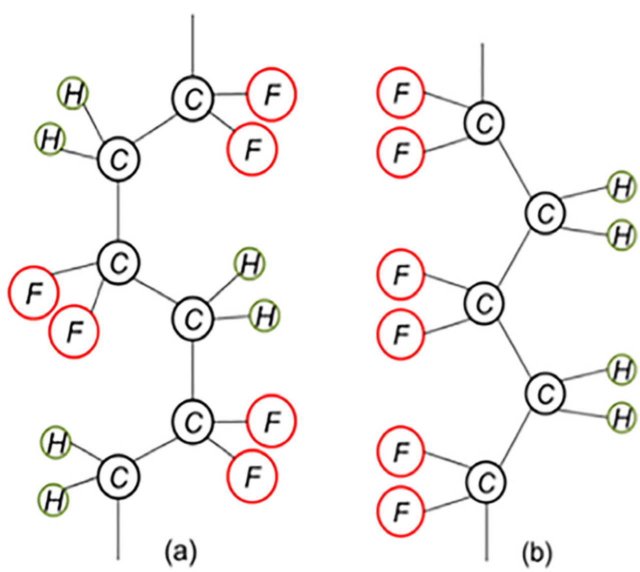


Fig. 1 Structures of α phase (**a**) and β phase PVDF (**b**): H hydrogen, C carbon, and F fluoride

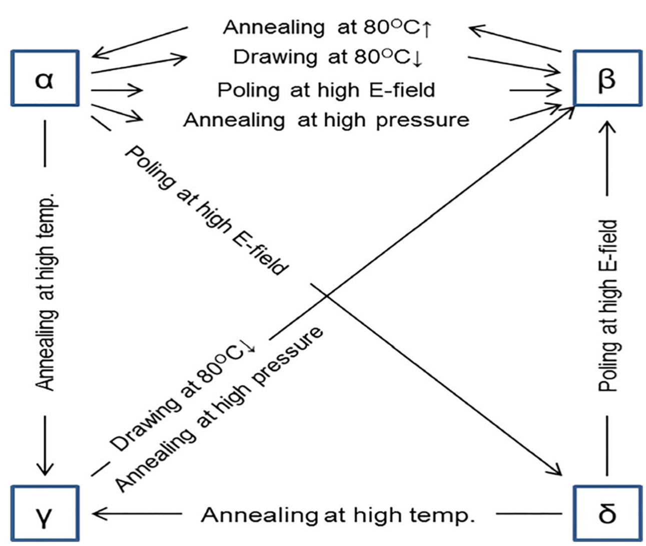


Fig. 2 The crystalline phase transformation diagram of PVDF polymer [2]

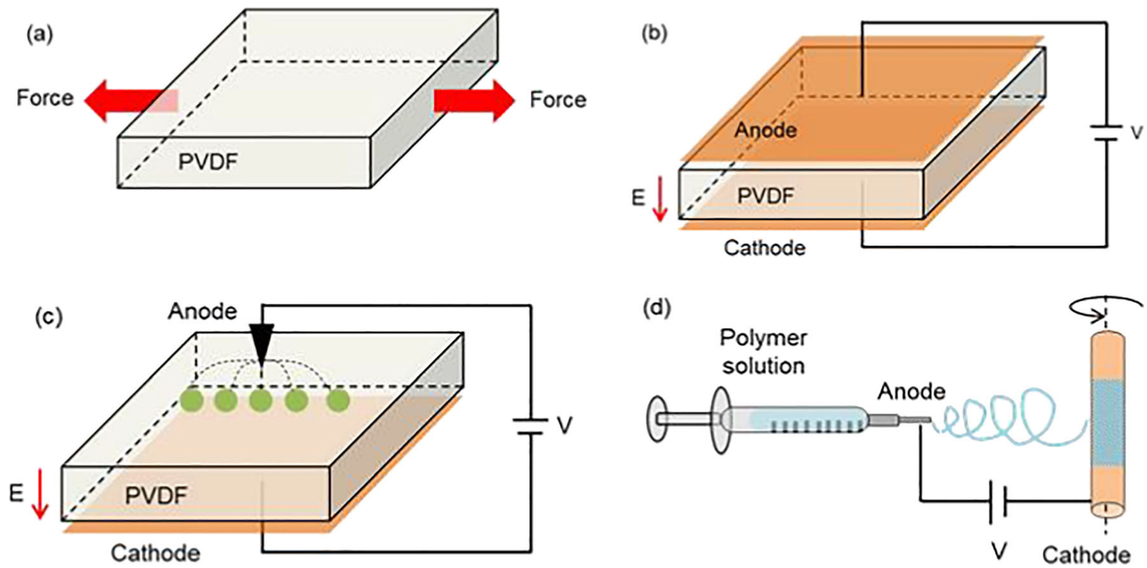


Fig. 3 Piezoelectric polymer processes: **a** mechanical stretching, **b** contact poling, **c** corona poling, and **d** electrospinning process

PVDF fibers from PVDF solutions in the presence of an electrical field but cannot be used to fabricate large areas. Moreover, the current outputs of devices produced with arrays of electrospun fiber of PVDF are less than 5 nA and the voltages are in the range of 1~20 mV [2, 7, 8, 11, 12]. Realistic device functionality under small mechanical motion can be achieved only by combining high volumetric densities of aligned arrays of fibers. In most researches, PVDF film or fiber has been focused due to lack other PVDF manufacturing processes, and the electric poling field strength is limited to air breakdown voltage [13].

2.2 Electric poling-assisted additive manufacturing process

A recent study introduced a completely transformative manufacturing process that integrates stretching and polymer poling processes into a 3D printing process [2]. The new manufacturing process enables producing a continuous piezoelectric PVDF polymer fiber with β phase conformation. A fused deposition modeling (FDM) machine was modified to apply a high voltage (HV) between the nozzle tip of the extruder and printing bed while printing as presented in Fig. 4. Similar to general FDM printing mechanisms, the extruding motor feeds the filament. Also, two cartridge heaters that are current-controlled were placed around the barrel to melt down the filament extruding through the nozzle tip. The PVDF polymer filament melts and the molten polymer is extruded through the nozzle tip by the extruder motor. A strong electric field is applied causing dipole alignment of the crystalline β phase of the polymer between the nozzle tip and printing bed. To make a printing bed heater electronically isolated from HV, the glass plate (3-mm thick) was installed. The diameter of the fiber can be adjusted by designing the geometry of nozzle tip hole and controlling the extrusion feed rate. In this direct printing process, three PVDF poling methods (mechanical, electrical, thermal) are applied at the same time while printing. The combined mechanical-thermal-electric poling can be

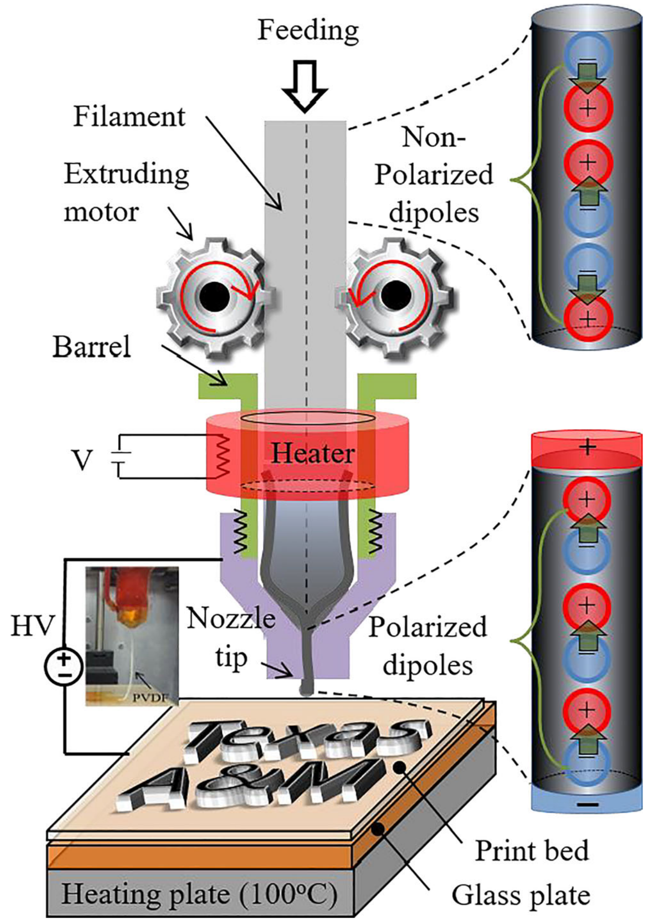


Fig. 4 A schematic of EPAM process

achieved by controlling the printing speed, melting the filament by heaters, and applying high voltages between the nozzle and printing bed at the same time as printing the piezoelectric polymers.

3 Experiment and results

PVDF sensors and actuators fabricated by electric poling-assisted additive manufacturing (EPAM) process are shown in Fig. 4. PVDF filament with a diameter of 3 mm was drawn from pellets by using a micro-compounder because ϕ3 mm PVDF filament is not commercially available. In this process, an extruder motor feeds a pure PVDF polymeric filament to an extruder that is heated up to 230 °C (PVDF glass transition temperature, 160 °C). The printing bed temperature is set to 100 °C to avoid thermal shock that may cause crack or deformation. The PVDF polymer filament melts and the molten polymer is extruded through the nozzle tip by the extruder motor. In this experiment, the nozzle size was chosen as 0.3 mm, which is the most commonly used in FDM printing processes, and the printing gap between the nozzle and printing bed was set as 0.3 mm. To keep the printing gap constant, the printing bed was leveled.

The sample with the size of 50 mm by 50 mm, 100% filling, and 0.3 mm thickness was printed under 2 mV/m electric field condition. From the previous study [2], it was found that the stronger electric field is applied, the higher piezoelectric outputs can be achieved. However, printing under more than 3 mV/m electric condition was difficult to control the electric breakdown while printing. This electric breakdown caused the printing surface damage, so the electric field condition 2 mV/m was determined. The filament feed rate and extruder feed rate were 30 mm/min and 200 mm/min, respectively.

The printability of PVDF highly relies on the surface energy of printing substrate that is in contact with PVDF extruding from the nozzle. Typically, PVDF surface energy is lower when the temperature increases. It indicates that PVDF extruding from the nozzle may not adhere on the printing bed. In this study, Kapton tape, glass (smooth), glass (rough), Cu, Al, and spray adhesive were used to find the best printing substrate for PVDF printing. PVDF did not adhere to Kapton tape, glass plates, Cu, and Al, but worked for spray adhesive.

FTIR (Galaxy series FTIR 5000) was used to obtain an infrared spectrum of absorption of PVDF samples fabricated by AM process under different electric poling conditions and to identify the PVDF polymer crystalline phase with respect to electric poling conditions as shown in Fig. 5. Spectra of absorption of three PVDF polymer samples were measured. First, the raw PVDF pellet was measured as a reference. Then, two printed PVDF polymer samples were measured. The samples fabricated

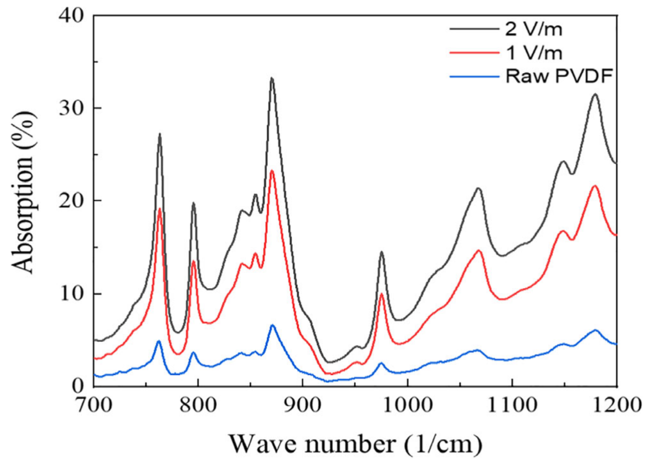


Fig. 5 FTIR results

under a high electric field demonstrated significant peaks at wave numbers 874 cm^{-1} and 1178 cm^{-1} which are both known as crystalline β phase that is responsible for the piezoelectric property of the polymer. It was found that the β phase peaks become sharper as the electric field is stronger.

3.1 Sensing test

The fabricated PVDF device was tested for force sensing applications as depicted in Fig. 6. Because the PVDF device output is a form of charge, the charge amplifier that is an

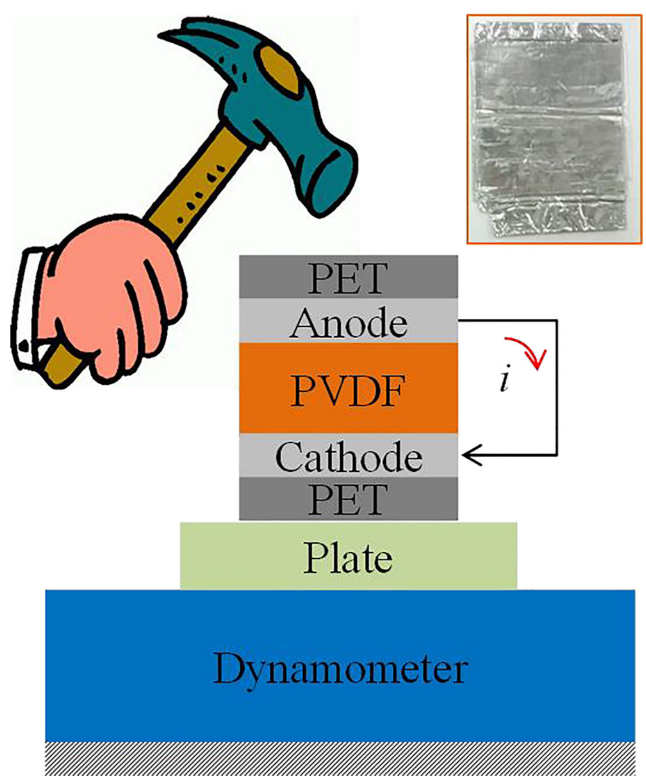


Fig. 6 Schematic of force measurement

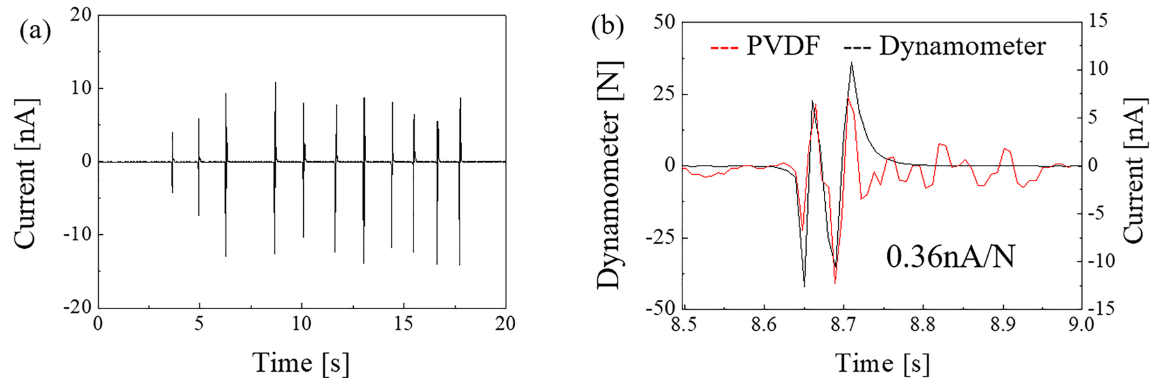


Fig. 7 Force measurement results: **a** PVDF force sensor output when tapping and **b** comparison of two force sensor outputs

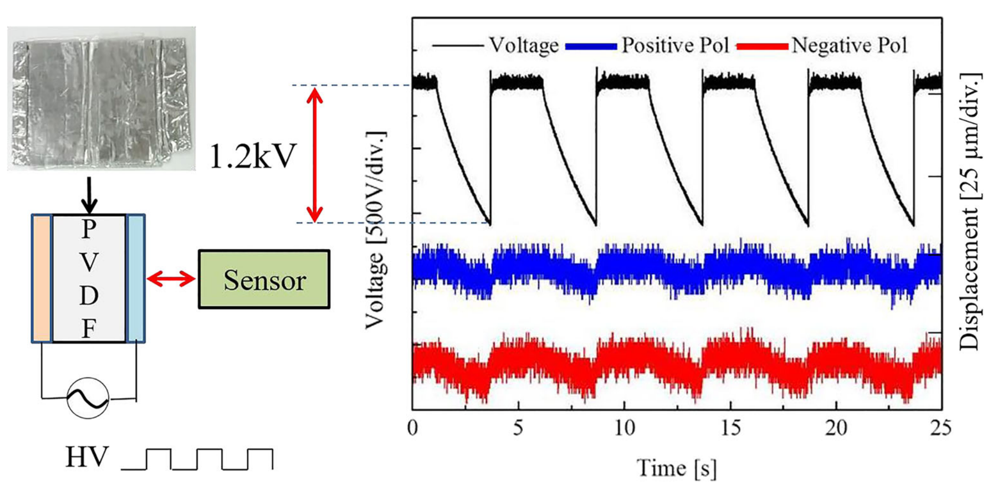
electronic current integrator was used to obtain a voltage output proportional to the integrated value of the input current. The voltage/current meter (Keithley) was used to obtain the current flow through the PVDF force sensor. Also, the dynamometer (Kistler) was used for a baseline comparison with the PVDF force sensor.

The impact hammer was tapped on the PVDF force sensor with a certain time interval. The outputs of PVDF force sensor and dynamometer were simultaneously collected with a National Instrument data acquisition board. Two force measurement results were shown in Fig. 7. Upon tapping, the peak current which could be found in Fig. 7a, b shows that PVDF force sensor output presented a good agreement with that of dynamometer. The force was measured by the dynamometer and the current produced from the PVDF device was measured by the current meter. From Fig. 7, the PVDF performance in ampere was calibrated with respect to the force applied to the PVDF device. The PVDF force sensor gain was estimated approximately 0.36 nA/N. The random ripples were measured because of PVDF polymer material deformation-recovery process after impact. It would be removed if the experiment is performed under a certain pre-load condition as similar as the dynamometer.

3.2 Actuation test

In addition to sensing applications, the PVDF device was tested for actuation applications based on the converse piezoelectric effect. As shown in Fig. 8, an external electric field 1.2 kV was applied between PVDF electrodes and a strain field, that is displacement information, was measured by capacitive displacement sensor that non-contact measures the gap between the PVDF actuator and sensor. One side of the PVDF actuator was fixed to form a cantilever, and the displacement was measured by applying the square wave electric field. The National Instrument data acquisition board was used to control the high voltage and to collect displacement information of the PVDF actuator. As seen in Fig. 8, the high-voltage power supply has large time constant that it took time to discharge on a control signal off condition. The high-voltage polarity effect of the PVDF actuator was performed by applying the high voltage to the PVDF actuator in positive and negative directions, respectively. The result showed that approximately 3 μm and 10 μm displacements were measured in the positive and negative polarity conditions, respectively. Because the PVDF actuator was printed under high-voltage polarity condition (negative polarity is the same direction with electropoling direction.), the relatively large displacement was

Fig. 8 PVDF actuation test result



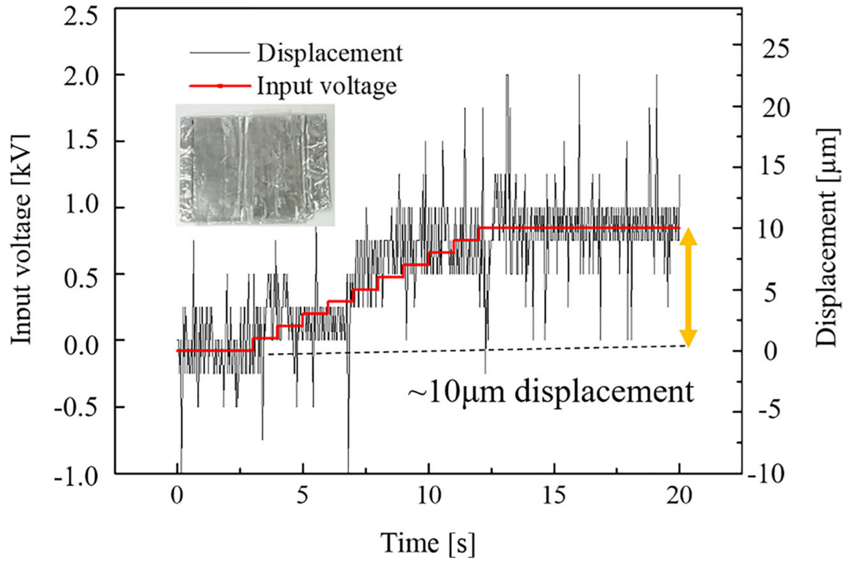


Fig. 9 Open loop PVDF actuator response to stepwise voltage input

achieved when the high voltage was applied in a negative polarity direction. The small displacement could be found even when the high voltage was applied in an opposite direction of electro poling because the untreated PVDF has a small portion of β phase peaks as seen in Fig. 5.

Also, displacement of the PVDF actuator was measured under a negative polarity direction while stepwise increasing the voltage from 0 to 1 kV as seen in Fig. 9. Although displacement was seen according to the input voltage, the motion of the PVDF actuator did not exactly follow the stepwise input voltage because it actuated in an open loop control. This nonlinear motion can be fixed by the closed loop control algorithm.

4 Further consideration

As an early stage research, a plasma-assisted printing process (PAPP) as depicted in Fig. 10 was investigated to transform PVDF into aligned β phase to produce higher piezoelectric characteristics than the EPAM process (Fig. 4). The field emission was empirically studied to identify the location on the Paschen curve [3] that produces a stable plasma and to characterize material interactions between interfacing layers to quantify plasma effects on piezoelectricity. A few researchers have indicated that plasma treatment can change the surface characteristics of PVDF causing it to become more or less hydrophilic [14–16]. However, there is no

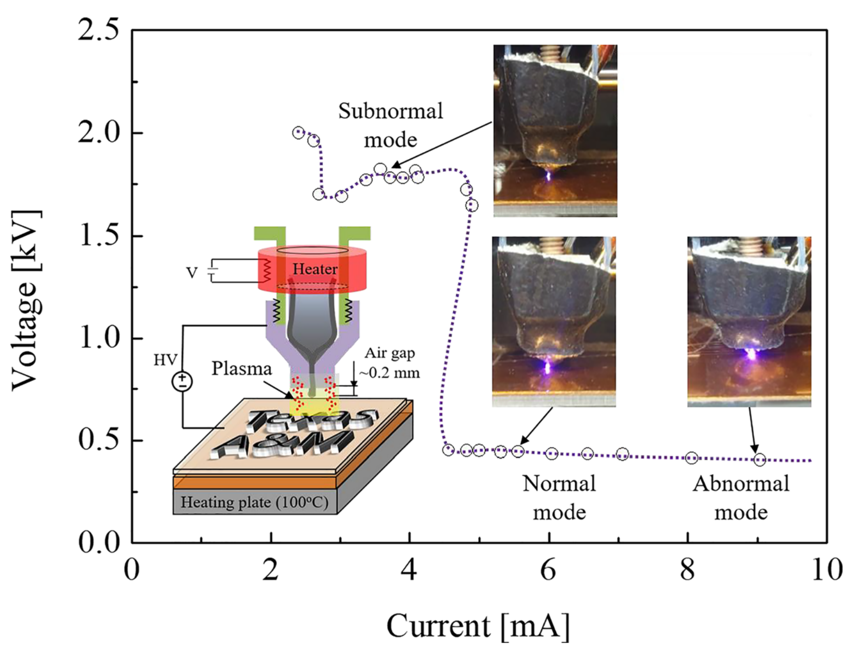


Fig. 10 Paschen curve and printing modes of PAPP

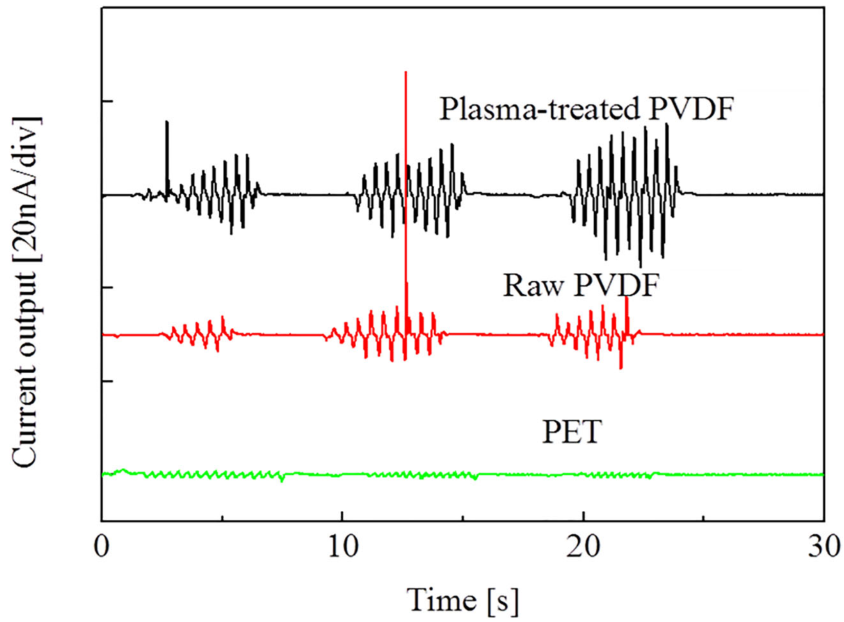


Fig. 11 Current measurement results of plasma-treated PVDF device

documentation about PVDF plasma treatment for piezoelectric performance enhancement. Here, printing modes and points on the Paschen curve resulting in a stable plasma that deposits significant ionic species on the material surface to increase piezoelectric properties were preliminarily studied. The Paschen curve was obtained by measuring the electric breakdown voltage while slowly increasing the current under 0.2 mm gap condition between the nozzle and printing bed. In a subnormal mode condition, the breakdown voltages varied, which indicates that it would be difficult to control or print the PVDF in a stable condition. Also, in an abnormal mode condition, the plasma resulted in burning the PVDF material and making burning spots on a printing bed due to high electric energy flow between the nozzle and printing bed as seen in Fig. 10, while there was no burning spot and the breakdown voltage remained constant in a 5–7 mA region in a normal mode condition. Based on the Paschen curve, the printing conditions were determined: gap 0.3 mm, current limit 6 mA, electric breakdown voltage approximately 480 V.

Due to lack of precision in FDM printer's linear motions, the gap between the nozzle and printing bed cannot remain constant during printing PVDF material under plasma conditions. As an early stage research, thus, PVDF films (50 mm by 50 mm) were prepared and attached on the printing bed, and then, the extruder passed over the PVDF films under gap 0.3 mm and current limit 6 mA conditions. The electrodes were attached on the plasma-treated sample, and the current was measured by folding the plasma-treated PVDF film. Also, the current produced from raw PVDF film and PET film by folding them was measured for the comparison as shown in Fig. 11. The PET film did not produce any current, and the plasma-treated PVDF sample showed 3~4 times better performance than the raw PVDF sample. This result indicates that the PAPP can significantly increase the direct printed PVDF piezoelectricity. This direct printing process will be further studied by using precision linear motion and control equipment.

5 Conclusion

This paper showed that the proposed EPAM and PAPP have a potential to enhance the PVDF piezoelectricity over a large area in a single-step direct printing process comparing to conventional PVDF processes. The hybrid mechanical-thermal-electric poling based on EPAM could be achieved by controlling the printing speed, melting the filament by laser and applying high voltages between the nozzle and printing bed at the same time while printing the PVDF polymers. In particular, it was found that the plasma between the nozzle and printing bed can increase the piezoelectricity 3~4 times. Developing a printing machine with high precision positioning and control performance and the fabricated devices made of various piezoelectric polymer/co-polymer materials will further improve sensing, actuation and energy-harvesting performance boundaries.

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