Effects of In-Situ Poling and Process Parameters on Fused Filament Fabrication Printed PVDF Sheet Mechanical and Electrical Properties

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Abstract

Polyvinylidene fluoride (PVDF) is a polymer prized for its unique material properties, including a high resistance to corrosive acids such as HCL and HF and its piezoelectric potential based on the proper microstructure arrangement. In this work, the effects of fused filament fabrication (FFF) routine parameters on printed PVDF film properties were investigated using a variety of experimental methods. The influence of in-fill angle (0° , 45° , and 90°) on the effective Young's Modulus, Poisson's ratio, and yield strength were evaluated using tensile testing and a digital image correlation (DIC) analysis. The phase content, in particular the β -phase amount, within the semi-crystalline PVDF films was determined as a function of processing parameters using the FTIR method. Considered parameters included the extrusion temperature, horizontal speed, *in-situ* applied hot end voltage, and bed material. Results showed that higher β -phase content was associated with lower extrusion temperatures, faster extrusion rates, and higher hot end voltages. While all "as printed" films demonstrated little to no measurable piezoelectricity, PVDF films printed with a high β -phase content and subjected to a post-printing corona poling procedure showed a small, but consistent piezoelectric response. Based on a static deflection cantilever beam experiment, the d_{31} coefficient of the poled specimens was estimated at 1.19 pm/V.

Keywords: piezoelectric; 3D printing; additive manufacturing; polyvinylidene fluoride; PVDF

1. Introduction

Additive manufacturing techniques enable rapid prototyping of components with clever design routines and minimal post processing. Recent advances in the field of 3D printing include Carbon3D's CLIP technology for exceptionally fast printing [1], Functionalize F-Electric conductive filament with 0.75 ohm-cm resistivity, and additive manufacturing with glass [2]. Fabrication of 3D parts has not only found profitability in industrial scenes but recently fused filament fabrication (FFF) printers have become a home commodity due to reduced cost and expired patents. Any added ability to 3D fabrication methods enhances rapid prototyping commerce and bolsters human creativity.

Smart sensing materials that are compatible with additive manufacturing techniques can be exploited to augment parts with sensing, actuation, or charge generating capabilities. Polyvinylidene fluoride (PVDF) is a pseudo crystalline polymer that is piezoelectric if processed under conditions that produce the proper microstructure. The TGTG' α -phase is the most energetically stable, but possess very weak piezoelectric properties when compared to the highly polar TTTT β -phase. Some methods of creating piezoelectric PVDF include hot pressing [3], stretching [4] [5] [6], Langmuir-deposition methods [7], and electro-spraying [8]. When fabricating PVDF sheets in the thin film regime (< 10 microns) through gel casting, β -phase content can be controlled by solvent type, spin speed, drying temperature, humidity, pressure, and annealing temperature/atmosphere [9] [10].

Three-dimensional construction of small piezoelectric polymer structures using digital projection printing has been investigated by Kim, *et al.* [11]. In their work polyethylene (glycol) diacrylate (PEGDA), barium titanate (BaTiO_3 , BTO), and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) were combined to form μm size structures. Non-patterned films had a piezoelectric d_{33} of 39 pC N^{-1} after poling, though the geometry of the films was not specified. Lee *et al.* investigated electric poling-assisted additive manufacturing (EPAM) with PVDF [12]. By applying a voltage to the hot end of a 3D printer, Lee's group was able to acquire individual piezoelectric PVDF extrudate fibers that generated charge when flexed. In addition, Bian, *et al.*, created a PVDF covered metal molybdenum fiber, electrically poled the structure, and then used the fiber as an air flow sensor [13]. Voltage responses for Bian's 10 mm long 0.4 mm diameter fibers were in the 100's of μV range for air flow rates of 0 to 18 m s^{-1} . Saari, *et al.*, enabled sensing and actuation by directly encapsulating conductive wire into a molten flexible plastic via a fiber feeding mechanism [14]. This allowed for in situ construction of coils that, as the author points out, could be enhanced further by 3D printing magnetic materials.

Bandyopadhyay *et al.* [15] created piezoelectric composites and ceramics utilizing three different rapid prototyping techniques; fused deposition of ceramics (FDC), lost mold, and soft tooling. FDC processing incorporated 50-55 volume percent PZT-5H into 1.75 mm filament that was then used to print green ceramic structures. Lost mold fabrication was done by printing a negative with a typical thermoplastic polymer, filling it with a PZT slurry, and then allowing it to dry. Soft tooling required 3D printing of the original part, making a silicone RTV mold of that part, injecting the mold with a thermoplastic binder loaded with PZT-5H, and then letting it cool before removing the part. All samples were processed at $500\text{-}550^\circ\text{C}$ to remove binder and then sintered at around $\sim 1,300^\circ\text{C}$. Sintered parts were filled with epoxy, electroded, and corona poled at 25 kV and 70°C for 15-20 minutes. Bandyopadhyay measured a d_{33} of up to 550 pC/N using these fabrication methods.

Gaytan *et al.* [16] fabricated piezoelectric barium titanate (BaTiO_3) parts by jetting a binder material over fine powder BaTiO_3 , sintering the parts, and then poling the resulting

samples in an oil bath for two hours at 2 kV/cm and 120°C. Although shrinkage values were high, specimens sintered at 1400°C showed a high d_{33} coefficient of 74.1 pC/N.

Unlike other common piezoelectric materials, PVDF does not require high processing temperatures [17] when compared to electroceramics like PZT (~600°C+) and can be extruded instead of sputtered like aluminum nitride [18]. The processing melt temperature for PVDF is on par with current open source FFF processes 170-200°C [19]. PVDF homopolymer is also relatively inexpensive when compared to other fluoropolymers [20], making it an ideal candidate for commercial and hobbyist printing material.

In this research, 3D printed FFF PVDF thick films are fabricated under different processing parameters, including in situ electrical poling. A custom hot end is constructed so that a high electric field can be applied between the brass nozzles and the grounded bed. In addition, select specimens are subjected to a post-printing corona poling procedure to probe for potential piezoelectric performance enhancement. Properties for the thick PVDF films are evaluated through tensile testing, FTIR characterization, and piezoelectric response measurements.

2. Experimental Methods

2.1. Equipment and Materials

A Reprap Prusa i3 fused filament 3D printer has been modified to accommodate a high voltage on the hot end mechanism and a ground plane on the construction bed platform. The thermistor on an E3D v5 hot end is electrically isolated by applying Kapton tape around any exposed metal leads. The glass part of the thermistor is then placed on the outside of the heating block and then insulated using fiberglass insulation tape and a generous amount of Kapton wrapping. A glass plate 3mm thick is covered in Fasson 2" aluminum duct tape with connecting conductive copper tape strips. Before applying an adhesion/electrical isolation layer of Kapton (50 μ m thick) or 3M Scotch Blue Painter Tape (110 μ m thick), the ground plane is tested for continuity. All surfaces were cleaned using an acetone, 2-propynol, and DI water routine. Additional extruder specifications are shown in **Table 1**.

Table 1. Extruder specifications.

Specification	Value(s)
Hot End Type	E3D v5
Thermistor Location	Side of Heat Block
Nozzle Geometry	Sharp & Flat Bottom
Nozzle Diameter (mm)	0.35
Max Voltage, Kapton Bed (V)	1750
Max Voltage, 3M Bed (V)	1000
PVDF Filament Diameter (mm)	1.75 $\pm$ 0.15

Homopolymer PVDF (Kynar 740) resin pellets were obtained from Trident Plastics Inc. and extruded in a solvent cleaned Filastruder that processed the plastic at a temperature of 220°C which gave a fairly consistent 1.75 $\pm$ 0.15 mm filament diameter. Since the filament was air cooled the filament tended to be oval and not purely cylindrical. To purge and clean the system, 20 meters of filament was processed until the PVDF was a consistent semitransparent white

color. Afterwards a spool of 250 grams was produced to be used in the following experiments below.

Extrusion of the PVDF filament was performed using a direct drive extruder and an E3D hot end via two different types of nozzles. One brass nozzle is conical and gave a good localized electric field across the molten PVDF film as it is extruded. The other brass nozzle was a custom flat head which was designed to give a very uniform electric field over the molten PVDF as the material was deposited. In addition, this custom nozzle aligned the molecular dipoles in the parts of the film already extruded as it traversed the applied sheet. Pictures of the modified grounded bed with Kapton, 3M tape, and the hot end with two different nozzle geometries are shown in **Figure 1**. Unless otherwise noted, an adhesive promoter (AquaNet) is used on top of the Kapton or 3M tape.

Figure 1. Grounded build platform with a) 25 μ m Kapton, b) 3M blue painters tape, c) hot end with flat nozzle, and d) hot end with sharp nozzle.

2.2. Mechanical Properties

Thin dog bone structures were printed under various parameters for mechanical property testing. Processing parameters varied included sample length, infill angle, and number of outside perimeters as shown in **Table 2**. Thicknesses for the grips of the printed sample are about twice the initial thickness. These dog bone structures are shown in **Figure 2a**.

Table 2. Samples used for mechanical property testing. All sample widths are 10 mm and extruded at 200°C.

Sample #	Length (mm)	# of Perimeters	Infill Angle (deg)	Sample Thickness (mm)
1	40	2	0	0.31
2	40	2	0	0.28
3	40	2	45	0.31
4	40	2	45	0.27
5	40	2	90	0.5
6	40	2	90	0.38
7	40	3	0	0.37
8	40	3	45	0.29
9	40	3	45	0.29
10	40	3	90	0.46
11	40	3	90	0.49

12	60	2	0	0.36
13	60	2	45	0.34
14	60	2	90	0.32
15	60	2	90	0.33
16	60	3	0	0.34
17	60	3	45	0.34
18	60	3	90	0.35

Upon printing, specimens were speckle patterned with black paint and allowed to dry for at least 10 minutes, **Figure 2c**. Each sample is loaded into a Shimadzu EZ-Test material testing apparatus, **Figure 2b**, that is equipped with a 500 N load cell. The crosshead rate (rate of grip separation) during tensile testing was 0.5 mm/min, during which high resolution images were acquired at a rate of 1 image per 6 seconds using a Nikon D3200. Standards for this test adhere to ASTM D882-10 except for a few notable exceptions. Crosshead rate was lower than typical standards due to low image capture rate capability. Initial grip separation was under the 250 mm specified for Young's Modulus evaluation because of bed construction area limitations.

Figure 2. a) Schematic of dog bone 3D printed PVDF samples, b) Shimadzu EZ-Test, and c) sample speckle pattern.

For each specimen, the effective mechanical properties of the printed PVDF films were found in two ways. In the loading direction, the average normal stress within the gage area was assumed to be $\sigma_{avg} = F_{load}/A_{cs}$ where F_{load} was the force value reported from the load cell and A_{cs} was the cross sectional area of the sample. Strain in the loading direction was estimated using crosshead displacement and assuming that deformation occurred only in the gage region. From the slope of the stress-strain curve the Young's Modulus was estimated.

In addition, a 2D digital image correlation (DIC) analysis performed on the images of the deformed specimens was used to more accurately compute both axial and transverse strains. Speckle pattern images were loaded into a 2D-DIC software package to compute the in-plane strains (ϵ_{xx} , ϵ_{yy} , ϵ_{xy}) throughout the linear elastic loading regime. From these strains Young's Modulus and Poisson's ratio were evaluated.

It should be noted that the material properties found herein are the effective mechanical response of the printed PVDF film components. The directionality of the infill angle was

expected to greatly influence the measured stiffness and yield stress. In addition, the cross-sectional area was assumed to be a uniform rectangular section, when in reality there exists a small degree of irregularity in the geometry due to the printing process. Overhead microscope images for a 0 and 45 degree infill untested sample are shown in **Figure 3** below.

Figure 3. Overhead Microscope images of a) 0 and b) 45 degree infill untested sample.

2.3. Processing Parameter Effects

Since PVDF's piezoelectric response is primarily dependent on the amount of crystalline β -phase in the films [21] [19], it is important to determine the β -phase constituents as a function of chosen process parameters. The key desired outcome is primarily a well-bonded layer with appreciable β -phase; a secondary goal is to have the dipoles aligned right after 3D printing. Parameters investigated include extrusion temperature, bed material, nozzle geometry, horizontal extrusion speeds, extrusion material multiplier, and extrusion direction effects. As stated above, the nozzle geometry should affect the immediately extruded plastic and the PVDF around it by allowing for a larger field area across the polymer over a longer period of relative time. For this reason the flat nozzle was chosen as the default constant in the initial parameter effect evaluation experiments. The extrusion multiplier (EM), or the modified amount of plastic being forced through the nozzle given a constant speed and deposition height, was also investigated. Results from previous studies suggest the higher the pressure on the extruded PVDF, the more crystalline [22] [23], and possibly higher concentration of β -phase [24] in the PVDF films.

Another effect that will be analyzed is the extrusion direction. Typical slicing profiles render a zigzag fill as shown in **Figure 4a**. There is a possibility that a one-way extrusion, **Figure 4b**, might give a better response due to aligned dipoles (longitudinal) being in the same direction for each line laid down. The first test was to see if it effects the amount of β -phase in the filament.

Samples printed for the purpose of testing piezoelectric properties was initially performed using 1x1" swatches, **Figure 4c**. They are ~0.2 mm thick and are always printed on an undisturbed part of the bed that has an adhesion promoter spray. After each sample is fabricated, it is cleaned using acetone, 2-propynol and DI water to remove the adhesion promoter, then dried

using an air gun. **Table 3** shows initial experiments to determine the effects of FFF processing parameters on the formation of β -phase in the PVDF samples.

Table 3. Initial parameter effect evaluation experiments.

Effect	Variable Change	Constants
Hot End Temperature	160° - 200°, by 10°C increments	Flat nozzle, Kapton coated bed at 100°C, 1x EM, 10 mm/s, poled 1,750 V
Bed Material	Kapton at 100°C and 3M tape at room temp. Poled and unpoled	Flat nozzle, Hot End at 200°C, 1x EM, 10 mm/s
Nozzle Type	Sharp versus flat brass nozzle, poled and unpoled	Kapton coated bed at 100°C, Hot End at 200°C, 1x EM, poled 1,750 V
Horizontal Extrusion Speed	3, 10, 20, 30, 40, 50 mm/s	Flat Nozzle, Kapton coated bed at 100°C, Hot End at 200°C, 1x EM, poled 1,750 V
Extrusion Multiplier	0.75, 1, 1.25, 1.5x	Flat nozzle, Kapton coated bed at 100°C, Hot End at 200°C, 10 mm/s, poled at 1,750 V
Zigzag vs One-Way-Extrusion	Rectilinear fill versus extruding one direction constantly, poled and unpoled	Flat nozzle, Kapton coated bed at 100°C, 1x EM, Hot End at 200°C, 10 mm/s

Figure 4. Extrusion method variations tested, including a) zigzag and b) one-way print routines, c) 25x25 mm and d) 100x25 mm film swatch specimen sizes.

Once a set of processing parameters lent satisfactory films, samples were fabricated and aluminum electrodes were sputtered/applied for piezoelectric performance characterization. Satisfactory will have a respectable β -phase, smooth surfaces on the top and bottom, and have minimal porosity so the electrodes do not short. Porosity in this case refers to gaps between PVDF extruded polymer paths or accidental breaks due to poor plastic adhesion.

Along with the 3D printed specimens, reference samples were also prepared from baseline materials (manufacturer's PVDF resin pellets, the extruded filament, etc.) to determine the influence of the 3D processing parameters on PVDF microstructure. These reference samples include the raw PVDF resin pellets, the extruded 1.75 mm filament processed at 220° C, strained pellets/filaments, and strained and corona poled extruded strips. Images of the baseline material are shown in **Figure 5a**. A simple vice was used to crush the resin and filament so that it underwent a highly strained process.

In addition to the baseline tests, select 3D printed films were also post-processed using mechanical stretching while under an electrical field. Swatches were cut to size so that they could be strained and corona poled, **Figure 5b**. Corona poling required a heated bed at about 80° C, a pulling rod to strain the material, and a steel needle at 7.8 kV placed 10 mm above the sample, **Figure 5c**. As the material is strained under high electric field, some of the α crystalline phases convert to β -phase while β -phase dipoles are induced to align with the applied electric field at the same time. Poled and processed samples are shown in **Figure 5d**.

Figure 5. a) PVDF reference samples, b) test swatches before poling, c) corona stretch and pole station, and d) swatches after stretch and poling.

2.4. Piezoelectric Properties

To estimate the piezoelectric coefficients of selected samples, unimorph specimens are constructed using PVDF as the top active layer and steel shim stock as the passive bottom layer, with an adhesive in-between. The equations determining the small static deflection of a unimorph (neglecting the adhesive layer stiffness) are derived using the method from [21]. A schematic of the beam is shown in **Figure 6a**. For a fixed width w and knowing that the post deflection must be in static equilibrium, the sum of the forces and moments must equal zero

$$F_x = w \int_{z_0}^{z_i} \sigma_x(z) dz \quad \text{Eq 1}$$

$$M_o = w \int_{z_0}^{z_i} \sigma_x(z) z dz \quad \text{Eq 2}$$

where $\sigma_x(z)$ is the x stress profile through the height of the beam. The stress profile for the piezoelectric and substrate layer are

$$\sigma_p = E_p \left(\varepsilon_0 z - d_{31} \frac{V}{h_p} \right) \quad \text{Eq 3}$$

$$\sigma_s = E_s (\varepsilon_0 z) \quad \text{Eq 4}$$

where ε_0 is the strain slope for the unimorph, E_p and E_s are the Young's modulus for the piezoelectric and substrate layer respectively, d_{31} is the piezoelectric strain coefficient, V is the voltage applied to the piezoelectric layer, and h_p is the thickness of the piezoelectric layer. The equation for deflection as a function of position along a unimorph beam length is

$$\delta(x) = \frac{3E_p d_{31} V E_s h_s (h_p + h_s)}{E_p^2 h_p^4 + 4E_p E_s h_p^3 h_s + 6E_p E_s h_p^2 h_s^2 + 4E_p E_s h_p h_s^3 + E_s^2 h_s^4} x^2 \quad \text{Eq 5}$$

where h_s is the height of the substrate layer and x is the position of the horizontal part of the unimorph. This method of constructing a relation between d_{31} coefficient and static displacement will be used to evaluate piezoelectric coefficients.

Figure 6. a) Schematic of unimorph beam, b) image of commercial test beam, c) 20x microscope image showing post voltage deflection.

3. Results

3.1. Young's Modulus and Poisson's Ratio

The stress versus strain curves derived from the Shimadzu material testing machine are shown in **Figure 7** for each infill angle. Engineering strain was calculated in the linear region for every sample via the Shimadzu load cell/displacement method and the 2D DIC method. From these values Young's Modulus is evaluated. Poisson's ratio is derived using the 2D DIC method only.

Figure 7. Stress-strain graphs derived from Shimadzu machine for various infill dog bone PVDF structures. Solid lines represent 40mm specimens, while dashed lines are 60mm.

From **Figure 7** ultimate stress is, on average, lowest in the 90 degree infill samples, though the 0 and 90 degree infill have about the same stiffness response. Results from the DIC package analysis are shown in **Figure 8** for a 0 degree angle sample. The sample is under 6.1 N of tensile load (about 1.7 MPa of stress).

Figure 8. 2D DIC results for tensile testing of a 0 degree angle under 6.1 N of force. Results for a) v (vertical) displacements, b) u (horizontal) displacements.

Table 4 shows the calculated Young's Modulus and Poisson's ratio for the three tested infill angles. The number of 3D printed perimeters did not seem to have a trending effect on any of the mechanical properties. The length of samples had an effect as the infill angle went from 0 to 90 degrees as shown by **Figure 7**. Measured Young's Modulus values for single layer test strips are lower than reported from literature: 3 GPa [25], 2.8 GPa [26], 2.5 GPa [27], and 1.7 GPa from Kynar 740 datasheet. It should be noted that the Kynar 740 bulk Modulus of Elasticity was measured at 1 mm/min which is twice the crosshead rate of our test specimens. Another important fact the reader should be cognitive of is that the number of samples tested in this research is below that which are needed to make these results statistically viable.

Table 4. Shimadzu and DIC results for Young's Modulus and Poisson's ratio for all dog bone structures tested.

Infill Angle (deg)	E_{Shimadzu} (MPa), Average	E_{Shimadzu} (MPa), Standard Deviation	E_{DIC} (MPa), Average	E_{DIC} (MPa), Standard Deviation	ν_{DIC} , Average	ν_{DIC} , Standard Deviation
0	484	50	497	41	0.243	0.064
45	481	78	545	165	0.361	0.060
90	419	100	429	84	0.310	0.063
All	457		486		0.305	0.062

Void spaces in the PVDF samples are ideally near zero due to specimen width calculations done during slicing. This is not realistically accomplished as the heights of each sample are shown to vary from **Table 2** above. Extrudate cross sectional area for the chosen slicing algorithm are described as a rectangle with rounded edges

$$Area_{extrudate} = (W - H)H + \pi \left(\frac{H}{2}\right)^2 \quad \text{Eq 6}$$

where W and H are the width and height of the extrudate with void spacing being

$$Area_{void} = H^2 + \pi \left(\frac{H}{2}\right)^2 \quad \text{Eq 7}$$

assuming that each of the extrudate areas are just touching. As the void area goes to zero then the spacing of extrudate pathing is

$$Spacing = W - \left(H - \frac{1}{4}\pi H\right) \quad \text{Eq 8}$$

which would create 0% total voids by volume, or the ideal case.

Estimation of trapped voids is done by weighing three of each infill sample (0, 45, and 90°), spraying all sample with a light and extremely thin sealant (Scotchgard Heavy Duty Water Repellent(3M)), immersing them in water and recording the volume displaced. With the original mass, volume displaced, and knowing the density of the filament prior to deposition, the percent of locked void spacing can be evaluated. While this will not evaluate ‘v’ crevices (surface roughness effects), it will give an approximation of how much air is trapped in the samples which may affect mechanical and electrical properties. The results for trapped air void % by volume is shown in **Table 5** below.

Table 5. Trapped air void % by volume

Fill Angle	Density (g/cm ³)	Filament Density (g/cm ³)	Void %
0	1.56 ± 0.07	1.78	12.36
45	1.67 ± 0.07	1.78	6.18
90	1.51 ± 0.03	1.78	15.17

3.2. Printing Parameter Effects on β -Phase

To estimate the relative amount of β -phase in each sample, Fourier transform infrared spectroscopy (FTIR) is performed using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Since the samples are relatively thick, an attenuated total reflectance (ATR) attachment is needed to obtain viable spectra. This means that only a certain amount of material on the surface can be analyzed. The ATR depth of penetration is defined as

$$p = \frac{\lambda}{2\pi \sqrt{(\sin \theta)^2 - \left(\frac{n_2}{n_1}\right)^2}} \quad \text{Eq 9}$$

where λ is the wavelength of light in the ZnSe crystal, θ here is the incident angle of light entering the sample (typically 45 degrees), n_1 is the index of refraction of the ZnSe crystal (2.4), and n_2 is the index of refraction of PVDF (about 1.4) [28].

In order to compare results of FTIR spectra, the scanned data had to be normalized because the peaks detected are a function of the amount of material in contact with the ATR crystal. To account for variability in contact area, a common peak in the samples spectra was identified so that each spectra could be normalized to it. The peak at 1070 cm⁻¹ was deemed consistent in amplitude so all other spectra were normalized to that peak. As it turns out, 1070 cm⁻¹ is independent of the three primary phases found in PVDF and has a linear relationship with the thickness of the sample in normal FTIR [29]. Since measurements are done using an ATR

adapter, the depth of absorption at that wavenumber is constant, thus why it was observed that 1070 cm^{-1} always had the same relative amplitude.

In **Figure 9** the raw and crushed Kynar 740 resin, raw and crushed extruded filament, the corona poled samples of **Figure 5**, and a 3D printed high β -phase containing sample from the initial parameter investigations are shown. Mechanically crushing the resin and filament in a vice increased β -phase (840 cm^{-1}) as expected when inducing high strains into the material. **Figure 9** also shows that as soon as the resin is thermally processed (via a filament extruder) the amount of α -phase increased greatly in the material ($760, 796, 974\text{ cm}^{-1}$). Wavenumbers identifying PVDF phases come from the Spectrum 100 software as well as [30], [31], [32].

Figure 9. FTIR-ATR normalized results showing absorbance peaks for raw and crushed resin and filament. Includes the unstretched and stretched corona poled samples. Also added in is a high β -phase content sample from the initial experiments.

Effects such as bed material, print speed, and temperature appeared to have an effect on the amount of β -phase in the samples. Conversely, zigzag, nozzle type, and extrusion multiplier did not produce any observable trends within the initial experiments. Bed material and in-situ poling were also found to have a small effect on the amount of β -phase in the samples, as shown in **Figure 10**. The Kapton #1 sample had 1,750 volts applied to the hot end while Kapton #2 did not. There was a subtle increase in the amount of β -phase for the poled sample. 3M sample #1 (blue painters tape) had 1,000 volts on the hot end and the 3M sample #2 did not. β -phase content seemed to be the same for the poled and unpoled 3M samples. The most significant finding here was that 3M tape gave more β -phase than the Kapton tape, even when poled at a lower electric fields.

Figure 10. The effect of bed material on the amount of PVDF β -phase.

Horizontal extrusion speed effects are shown in **Figure 11**. Faster extrusion speeds produce more β -phase than slower speeds. This has the tradeoff of decreased poling time for increased printing speeds, which may also affect dipole alignment for samples coming off of the build bed. Faster printing speeds also increase fluid pressure within the nozzle.

Speed Effect

Figure 11. The effect of speed on the amount of PVDF β -phase using the flat nozzle and Kapton tape.

Hot end temperature influence on β -phase is shown in **Figure 12**. Given the constants of the experiment, colder extrusions produce higher β -phase in the PVDF. Adhesion to the bed, and adhesions to the PVDF itself is lowered significantly though. Below 190°C the samples are so simple to pull apart that further experimentation below this temperature was abandoned.

Temperature Effect

Figure 12. The effect of extrusion temperature on the amount of PVDF β -phase.

The first round of parameter investigations showed that higher temperatures were required for good adhesion, that faster extrusion speeds on 3M tape increased β -phase, and that applied voltage potentially increased β -phase. A sharp nozzle also made smoother surfaces than the alternate flat tip and is a mandatory characteristic for applying electrodes. A second round of experiments were performed to test *in-situ* poling voltage and the processes effect on β -phase using the previous knowledge obtained. Samples at 30 mm/s, with a 3M tape bed, and a sharp nozzle are printed at different temperatures with and without nozzle voltage. Figure 13 below shows that an electric field applied to the PVDF does indeed enhance the amount of β -phase but only at increased temperatures.

Thus, samples printed at a speed of 30 mm/s, 3M tape as the adhesion material, a sharp nozzle at the higher temperature, and an applied voltage of 1000 V were evaluated for a piezoelectric response. Although the majority of experiments are performed with a flat nozzle the sharp nozzle extruder geometry was selected in the end as it produced the smoothest specimen surfaces, which was a consideration for electrode deposition.

Figure 13. *In-situ* voltage effects on the amount of PVDF β -phase.

Horizontal extrusion speed effects on the surface morphology (top side) of PVDF printed samples is shown in **Figure 14** below. These samples correspond to the FTIR-ATR results from **Figure 11** above. A general transition of surface morphology can be observed as the printing speed varies.

Figure 14. SEM images of the top surfaces corresponding to a) 3 mm/s, b) 10 mm/s, c) 20 mm/s, d) 30 mm/s, e) 40 mm/s, f) 50 mm/s feed rates.

3.3. Piezoelectric Coefficient Evaluation

To verify the piezoelectric response testing methodology, the piezoelectric coefficient for a commercially produced piezoelectric PVDF sheet was first evaluated. PVDF strips from

Goodfellow (FV301960/3, uniaxially strained, $d_{31} = 19 \text{ pC N}^{-1}$, $d_{33} = -20 \text{ pC N}^{-1}$, $110 \text{ }\mu\text{m}$ thick) were adhered to a steel shim stock ($50 \text{ }\mu\text{m}$ thick) using a thin industrial adhesive. As received, the commercial strips are sputtered with a 2 ohms/square film of aluminum as electrodes. The bilayer beam was clamped on one end, giving an effective length of 28 mm , with a width of 6.5 mm . Prior to piezo-response testing, the mechanical stiffness of the Goodfellow PVDF was also experimentally determined via tensile testing, giving an average Young's Modulus of 0.928 GPa .

During piezoelectric response testing, a voltage differential is applied across the active piezoelectric layer, inducing a deflection of the composite structure as described by Eq 5. Voltage differentials of 250V and 500V were applied to the unimorph beam while the tip deflection was recorded under an optical microscope. Images of the tip displacement were taken for multiple tests and used to compute the transverse piezoelectric coefficient, d_{31} . Based on these experiments, the d_{31} coefficient of the commercial PVDF was 19.4 pC N^{-1} , which is 2.1% higher than the manufacture specifications.

For the 3D printed PVDF strips fabricated in this work, three different types of electrodes were considered: physical vapor deposited aluminum, CircuitWorks CW2400 conductive epoxy, and Anders Product Wire Glue. The CircuitWorks epoxy adhered well but eventually became brittle and cracked even when the thinnest layers were applied. Sputter coated aluminum electrodes (300 nm) adhered well, but only when immediately preceded by a surface plasma treatment. An adhesion assisting plasma clean was done in 8 sccm nitrogen with an RF power source at 50 W for 2 minutes . Physical vapor deposition parameters for the aluminum are 300 W and 5 mTorr . The biggest downside to the aluminum deposition method was that it tended to find even the smallest gaps in the film, resulting in electrical shorts to the other side of the film, thus decreasing useful PVDF area. The most effective electrode material was found to be the Anders Wire Glue, which utilizes carbon as the conducting material. When mixed with deionized water and put down in thin layers, it adhered extremely well to the PVDF surface when dry. The sheet resistance of the Wire Glue was the worst of the other two materials at $500\text{--}1,000 \text{ ohm/square}$ but since PVDF tends to have a high optimum resistance [33] for energy harvesting compared to other piezoelectric materials this was deemed acceptable for initial coefficient evaluations.

After electrode application, the 3D printed PVDF films were evaluated for an initial piezoelectric response. This evaluation was performed by connecting the electrodes to an open circuit through an oscilloscope and monitoring the induced voltage response during rapid deformation of the composite beam structure. If there were substantial dipole alignment within the specimens after printing, then the beam would generate a decaying voltage sine wave. However, regardless of the printing parameters, none of the “as-printed” films tested demonstrated a significant voltage response. Instead, a post-print poling procedure to induce dipole alignment was required to produce a piezoelectric response within the PVDF films.

Samples selected for post-print poling were printed at 200°C , 30 mm/s , $1\times$ extrusion multiplier, with a sharp nozzle at $1,000 \text{ V}$, and a blue painters tape adhesion bed surface at room temperature, as these parameters were demonstrated to give higher β -phase content, good interlayer adhesion, and low surface roughness.

To avoid shorting during contact poling, two 3D printed PVDF strips (0.3 mm thick) were adhered back-to-back with JB Weld and allowed to dry. The laminate was cut 13.8 mm wide by 100 mm long. Carbon electrodes were applied to the top and bottom, keeping about a 1mm gap from the edges to prevent short arcing paths about the thickness. Conductive copper

tape connection tabs were put down near the end of the device for external connections. Then a steel shim (50 μm thick) was adhered using JB Weld to one side, making a unimorph.

During poling the unimorph is put into a canola oil bath at 80°C while a voltage setting of 300V was applied across the electrodes. After an hour, the voltage was ramped to 5 kV and held for 1 hour. The temperature of the canola oil was then brought down to room temperature, thus aligning the dipoles under a 8.33 MV/m electric field.

Since contact poling is performed in canola oil at 80°C, it is important to understand how JB Weld's stiffness is modified given the different conditions. Three strips of JB Weld were cured, one in air for one day, another in a 100 C oven for 1 hour, and lastly in canola oil at 80 C for 1 hour. Shimadzu tensile testing revealed a Young's modulus of 252 MPa, 999 MPa, and 733 MPa for air drying, 100°C oven, and 80°C canola oil respectively. A Young's modulus of 733 MPa will be used for the evaluation of piezoelectric coefficients. The thickness of JB Weld between the steel stock and PVDF was appreciable while the JB Weld between PVDF prints was not.

Post poling tests showed that the unimorph device generates a decaying sinusoidal voltage with an initial peak-peak response of $2V_{pp}$ given an oscilloscope impedance of 10 MOhm. Next the sample was put under the microscope and a voltage of 1 and 2 kV was applied. The deflections of 5.0 and 10.1 μm were observed for the 1,000V and 2,000V tests. Using a modified version of Eq 5 for a 3-layer beam, an average d_{31} coefficient of 1.19 pm/V was found for these specimens.

4. Discussion

Based on FTIR results, colder extrusion temperatures produced larger β -phase peaks at the expense of interlayer material adhesion. The film surfaces also tended to be rougher than higher temperature extrusions, which would be problematic for making continuous contact with a subsequently deposited electrode. Conversely, if the line widths were appropriately spaced, the surface of higher temperature extrusions could be made very smooth. With PVDF, if the extrusion line width is too compact (overlapping, thus to nullify void space) then the material tends to ride up on the previous line creating an out-of-plane wave that continuously propagates onto the proceeding lines. The authors attribute this effect to the high viscosity of molten PVDF [34], [35].

The effective Young's modulus for the 3D printed Kynar 740 was highest when the extrudate was parallel with the axial loading direction of the specimen. This result is expected as the continuous extrusion direction act similarly to the fiber orientation in composite materials. Similarly, the weakest direction for the 3D printed films was transverse to the extrusion direction. Poisson's ratio derived via DIC for the 0° case is also explained by the perpendicular forces causing fused zones to strain more, thus giving a lower Young's modulus. The overall lower Young's modulus values found for printed PVDF sheets (~0.4-0.5 GPa) compared to bulk literature values (1.7-3 GPa) is somewhat expected as the structure of the FFF printed sheets has a higher porosity than bulk specimens (in terms of gaps made by extruding line by line and trapped voids in the material itself). It is also reiterated that the number of samples tested for each variable is too small to make the results statistically significant.

The β -phase content of PVDF films was influenced most significantly by the deposition speed, hot end temperature, and bed material. Of these factors, printing speed was the most significant. While fast printing speeds likely induce more β -phase due to mechanical strains, a much slower printing speed may provide benefits related to the time that the printed material is

subjected to an electric field. Ideally, the material should be drawn at a high rate and remain under the poled electric field until it cools to a point where the aligned dipoles are unable to randomize. The flat nozzle setup was expected to resolve this issue, but was found to induce residual stresses sufficient to delaminate the PVDF film and curl onto the nozzle at higher speeds. If a better bed material could be used that would promote superior adhesion to that of hot brass, then flat nozzles might become viable. Currently the printing speeds used herein do not appear to provide sufficient time for the alignment of dipoles to occur for in-situ electrical poling during printing. This does not preclude alternative combinations of printing speed and electrical poling from potentially useable piezoelectric printed high β -phase PVDF films.

One potential avenue for reaching more efficient piezoelectric properties may be through higher applied electrical fields during printing, which were limited in this study by the current hot end set-up. Applying higher temperatures during electrical poling also increased β -phase. It is conceivable that much higher applied nozzle voltages coupled with higher temperatures would increase the piezoelectric potential and also expand the poling range of the hot end. One concern that arises when pushing the upper limits of the applied in-situ electrical field is arcing between the hot end and the grounded bed, which can disrupt serial communications between the computer and the printer. This issue was found to occur in this work at about 1,500 volts when using the 3M Blue Tape and about 3,000 volts when the positive electrode was touched to the Kapton tape. Any small rips or tears in the adhesion/isolation layer can cause immediate serial communication failure, so care was taken not to process on any worn portions of the bed.

FTIR-ATR results show that crystalline phases on the bottom of the PVDF samples have lower amounts of β phase, independent of the bed material choice. This is most likely because the PVDF sticks to the bed and is then unable to be strained at that surface. Thus β -phase content is most likely not constant throughout the layer height. Since the ATR only measures attenuation a small fraction into the surface, it is able to observe this effect. β -phase promotion via strain is theorized then to have a parabolic profile where the maximum β content is located at the top of the sample surface nearest the nozzle.

Like [36] promotion of β -phase relies on high pressures, stretching, additives, quenching, etc. Many of the results presented here follow the same trend, though many cannot be directly incorporated due to the nature of FFF additive manufacturing. Quenching the extrudate for example should help form more β but could also cause premature warping of the film because of high thermal coefficient of expansion values. Stretching is a difficult problem since the designed film, if it were to be incorporated with an autonomous multipart build, would be vastly different in geometry. Additives like salt and ceramics could be done at the filament construction phase and at this point seem like the next area to exploit.

Stretching of the films is not conventional in FFF printing but is, in a way, mimicked. As [37] shows for very thin α -films, stretching to ratios of up to five times the original length at elevated temperatures (80-140°C) give large amounts of β . Extrusion of PVDF filament does strain the material and higher feed speeds show larger β amounts. Which could mean that even faster feed rates would lend even more β -phase.

It should be noted that the copolymer poly[(vinylidene fluoride-co-trifluoroethylene)] or P(VDF-TrFe) has a high β -phase stable condition during solidification. It has been used in inkjet printing [38] and spin casted [17] sensors/actuators with great success. The largest disadvantage this copolymer has is cost, which sits at about \$4,600/kg currently (PiezoTech, Arkema). To put this in perspective, 10 lbs of Kynar 740 costs about \$300 (or \$66/kg) from Trident Plastics, PA.

Another potential path to higher β -phase parts is not through the processing of the final feed extrudate, but on the mechanical and thermal processing of the filament beforehand. Extrusion, quenching, and drawing of PVDF monofilament from [39] shows that high amounts of β -phase (~95%) are induced after processing. Though post processing the filament into a 3D printed form will significantly convert most of this β -phase to α via melting.

Similar to the efforts of [13], a post-deposition electrical poling was required to align the dipoles. Single layer samples could be post poled, though the area of poling was quite small. This was due to shorting between layers via small holes in the printed extrudate. To obtain an appreciable thickness to length ratio, a double-layered PVDF sample was made to create a unimorph. Poling voltages were considerably high but the thickness of PVDF means the electric field during poling is on the low side of conventional poling methods (~10 MV/m). If elimination of the small holes during printing can be achieved, then higher poling fields like 80 to 100 MV/m could be attempted, likely producing better piezoelectric coefficients.

5. Conclusions

Young's Modulus for the 3D printed PVDF samples are 457 and 486 MPa on average for Shimadzu and DIC experiments. Poisson's ratio was found to be an average of 0.305 using DIC. Yield strength was highest when the infill was aligned to the pulling axis and reduces with reducing infill angle. Poisson's ratio is lowest for single layer extrusions when the force is parallel with the extrusion path.

PVDF β -phase may significantly increase in 3D printed samples by stretching and poling under a corona field. Lower temperature extrusions of 170°C had very high β -phase content but interlayer adhesion was weak and had a rough texture. High temperature extrusion had lower β -phase but stronger adhesion and smoother textures if the PVDF line widths are appropriate.

Bed material, such as the 3M Blue Painters Tape, was more porous and gave more β -phase at room temperature in the samples versus the Kapton tape at 100°C. Breakdown voltage was about 1,000 volts using Blue Tape and printing samples at 250 μ m layer heights. The breakdown voltage for Kapton was not evaluated because arcing from the hot end to the thermistor lines happened first at 2,500 volts, which required a hardware exchange.

Higher horizontal speed extrusions increased β -phase. Smooth extrusions were only viable using the sharp nozzle due to bad adhesion and curling using the flat nozzle. Voltage enhanced β -phase content but only for the higher temperature samples. Applied voltage during extrusion did not align enough dipoles in the PVDF to obtain an appreciable charge during testing.

Electrical poling in an 80°C oil bath of relatively high β -phase content printed PVDF films at a field of 8.33 MV/m produced a repeatable, albeit small, piezoelectric coefficient d_{31} of 1.19 pm/V.

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