Solid Freeform Fabrication 2018: Proceedings of the 29th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference
Reviewed Paper

Influences of printing parameters on semi-crystalline microstructure of fused filament fabrication polyvinylidene fluoride (PVDF) components

Niknam Momenzadeh*, Thomas A. Berfield*

*Department of Mechanical Engineering, University of Louisville, Louisville, KY 40292

Abstract

Piezoelectric polymers have garnered wide interest for sensing, actuation, and energy harvesting applications due to their unique combination of high strain tolerance and electro-mechanical coupling. Compared to other piezoelectric polymers, polyvinylidene fluoride (PVDF) and its copolymer and terpolymer variations demonstrate some of the strongest piezoelectric responses. One of the primary challenges associated with PVDF is that its piezoelectric response is highly dependent on its microstructure, which varies greatly with manufacturing-associated stresses. This work investigates Fused Filament Fabrication (FFF) of PVDF polymers, and the effects of processing parameters such as layer thickness, infill pattern, infill density and nozzle diameter on its microstructure development. Fourier Transform Infrared Spectroscopy (FTIR) measurements are used to assess the relative phase content of the semi-crystalline microstructure arrangement primary related with significant piezoelectric response in PVDF (β-phase).

Keywords: Polyvinylidene Fluoride- Piezoelectric Properties- Fourier Transform Infrared Spectroscopy-Fused Filament Fabrication

Introduction

Piezoelectricity is a phenomenon that refers to the ability of some materials to generate an electrical potential in response to an applied force and vice versa. Large group of ceramics (such as Barium Titanate (BaTiO3), Lead Zirconate Titanate (PZT), Lithium Niobate (LiNbO3), Lithium Tantalate (LiTaO3)) and some select polymers (like PVDF, poly-L-lactic acid (PLLA), Polymethyl-L-Glutamate (PMG)) exhibit piezoelectric behavior [1, 2]. Piezoelectric polymers have garnered wide interest for sensing, actuation, and energy harvesting applications due to their unique combination of high strain tolerance and electro-mechanical coupling. Compared to other piezoelectric polymers, polyvinylidene fluoride (PVDF) and its copolymer and terpolymer variations demonstrate some of the strongest piezoelectric responses, therefore this biocompatible polymer is the most widespread piezoelectric polymer. PVDF is widely used in different commercial applications such as energy harvesting systems [3], tissue engineering [4], driving vibration [5], and as sensors and transducers [6, 7]. Thermal and chemical resistance of this thermoplastic polymer makes PVDF a good choice for use in different harsh environment and in direct contact with corrosive acids such as HF, HBr and HCl. When used as a binder in composites, PVDF has also shown resilience in abrasive wear applications [8]. The electro-mechanical coupling behavior of this piezoelectric polymer are highly linked to its microstructure. The microstructural phase is a function of the stress state and the thermal history experienced by the material during the deposition process. PVDF has five different polymorphs, of which, four structures have a net dipole. The β-phase demonstrates significant pyroelectric, piezoelectric, and ferroelectric response. Consequently, enhancing the amount of this polymorph within PVDF during manufacturing is a priority. Conversion from other phases into the β-phase can be achieved through a combination of pathways, but essentially via stress and temperature [9-11].

Material Extrusion Additive Manufacturing (MEAM) technique is one intriguing approach to induce piezoelectricity within additively manufactured PVDF components. However, due to the large coefficient of thermal expansion of PVDF that leads to unwanted disortions and poor surface bonding characteristics, 3D printing of this material by Fused Filament Fabrication (FFF) method is a bit challenging. Lee et al. [12] deposited individual fibers from extruded PVDF filaments under an in-situ electric field in order to fabricate freeform piezoelectric devices in a single processing step. Tarbuttona, et al. [13], demonstrated that phase transformation occurs in 3D printing of PVDF and the amount of α-phase (the most stable and abundant polymorph of this polymer) decreased while the β-phase content increased. Kim, et al. [14], used in-situ corona poling electric field to improve dipole alignment, and piezoelectric PVDF films with enhanced β-phase percentage were fabricated through this technique. Porter, et al. [15], showed that there is limited influence of the relatively small electric field compared to post-processing poling field effects on piezoelectric behavior and it was demonstrated by them that fabrication conditions with higher printing speeds, lower deposition temperatures and higher hot-end voltages improve the amount of crystalline β-phase in the material extrusion additively manufactured parts. In addition, according to their research, nozzle types (conical or flat) and extrusion multiplier has no significant effect on the piezoelectric responses of the fabricated components. The influences of other printing processing parameters such as infill density, fill pattern, layer thickness and nozzle diameter on the amount of β-phase content are still not determined.

In this research, an experimental study was done to define the influence of printing parameters (infill density, infill pattern, layer thickness and nozzle diameter) on β-phase crystallization content within the PVDF fabricated parts. Since the piezoelectric behavior of homopolymer PVDF is essentially related to the amount of β-phase polymorph [16], knowing the relationships between the aforementioned printing parameters and resulting β-phase content will clarify the viable processing parameters based on piezoelectric responses.

Experimental Methods

The raw material in this study which was provided from Trident Plastic Inc., was PVDF Kynar 740 which is received in the form of pellets. PVDF Filaments for 3D printing of the samples with open source FFF printer were fabricated from these raw pellets by utilizing a filament extruder at the temperature of 215°C. Inconsistent filament diameter can cause poor deposition performance, therefore controlling the quality of extruded filament is an aspect that should be considered. The diameter of the extruded filament for the entire length was 1.75 mm with tolerance of ±0.15 mm, which is precise enough to use in the material extrusion additive manufacturing 3D printer.

The fabricated PVDF filaments were fed into an open source 3D printer, Reprap Prusa I3, in order to print specimens. All the samples were deposited on a heated platform, because additional heat from plate will increase the bonding quality between the printed layers and build plate. The print bed was also coated with 3M blue painters tape to increase adhesion quality and produce print parts with less unwanted distortion compared to that of using Kapton tape or just a glass plate.

Multiple processing parameters were set at optimal value in order to print PVDF samples [17]. These values are critical aspects to have printed part with less warping and great layer to layer bonding. The fixed, optimal printing parameters are presented in Table1.

Table 1 – Deposition specification

Extrusion Specification	Optimal Values
Perimeters	2
Brim width (mm)	3
Deposition temperature (°C)	220
Bed temperature (°C)	100
Speed (infill and solid) (mm/s)	15
Speed (external perimeter) (mm/s)	10

In order to investigate the effect of infill density, infill pattern, layer thickness and nozzle diameter on the piezoelectric potential of printed parts, specimens were deposited in 6 different levels of infill density, 5 distinct patterns of printing, 4 different layer thickness heights, and 5 different nozzle diameters (Table 2). At least 3 samples were fabricated for each unique set of printing parameters. The thickness and diameter of all samples were fixed at 3mm and 20 mm, respectively. PVDF 3D printed samples were shown in the Figure1.

Figure 1- FTIR test samples

Table 2 – Specimens used for FTIR testing

Sample Variation #	**Infill density**	**Infill pattern**	**Layer thickness (mm)**	**Nozzle diameter (mm)**
1	100%	Rectilinear	0.10	0.4
2	95%	Rectilinear	0.10	0.4
3	90%	Rectilinear	0.10	0.4
4	85%	Rectilinear	0.10	0.4
5	80%	Rectilinear	0.10	0.4
6	75%	Rectilinear	0.10	0.4
7	90%	Concentric	0.10	0.4
8	90%	Honeycomb	0.10	0.4
9	90%	Rectilinear	0.10	0.4
10	90%	Grid	0.10	0.4
11	90%	Triangles	0.10	0.4
12	100%	Rectilinear	0.05	0.4
13	100%	Rectilinear	0.10	0.4
14	100%	Rectilinear	0.15	0.4
15	100%	Rectilinear	0.20	0.4
16	100%	Rectilinear	0.10	0.2
17	100%	Rectilinear	0.10	0.4
18	100%	Rectilinear	0.10	0.6
19	100%	Rectilinear	0.10	0.8
20	100%	Rectilinear	0.10	1

Fourier-transform infrared spectroscopy (FTIR) test is employed for measuring the amount of crystalline β-phase in the PVDF printed samples. The β-phase content is associated with significant piezoelectric responses. Hence, FTIR is a good technique for comparing the relative piezoelectric properties in PVDF specimens fabricated under different conditions. All samples were tested by a PerkinElmer Spectrum™ 100 FT-IR spectrometer with an attenuated total reflectance (ATR) attachment.

Results and Discussion

The stress state of homopolymer PVDF dictates the semi-crystalline polymorph content of PVDF. Higher β-phase content (associated with piezoelectric response) of PVDF will be varied using different printing conditions. The plots from FTIR characterization test characterize the phase determination in the fabricated PVDF. This material has notable vibration bands at 510 cm^{-1}, 840 cm^{-1} and 1278 cm^{-1} in the FTIR spectra which are unique to the β-phase. According to literature [18, 19], equation (1) was used for quantifying the results of the FTIR test in a manner that calculates the β-phase fraction within the printed components.

$$F(\beta) = \left(\frac{A_\beta}{1.26\, A_\alpha + A_\beta}\right) \qquad (1)$$

A_α and A_β represent the absorption band at 763 cm^{-1} (α-phase) and 840 cm^{-1} (β-phase), and F(β) corresponds to the relative fraction of β-phase in the fabricated samples. Intensity of vibrational bands are dependent on the amount of contact between the samples and the crystal in FTIR machine, therefore all the data from FTIR characterization tests were normalized to 1070 cm^{-1} in order to have the ability of comparing the scanned data [15]. Variations of F(β) for 3D printed PVDF samples using different deposition parameters was evaluated to determine the parameters influences.

Infill Density

Infill density is one of the processing parameters that has notable effect on the strength of the printed samples, which determines the volume portion of the part that is filled with printing feedstock material. Different percentages of infill density (100%, 95%, 90%, 85%, 80%, 75%) were used in order to clarify the effect of fill density on the piezoelectric properties. Figure 2 shows the fraction of β-phase in different percentages of infill density. Higher percentage of fill density leads to parts with more crystalline β-phase, which means the fraction of β-phase in the specimens printed with 100% infill density is higher than the others. Increasing the percentage of infill printed material from 75% to 100% will decrease the number of air gaps within the printed samples, and the residual stress state of the material. Therefore, the piezoelectric properties of FFF printed parts were directly tied to the infill density of printed samples. Although higher percentage of infill density consumes more material and printing time, it produces much stronger components with higher piezoelectric properties.

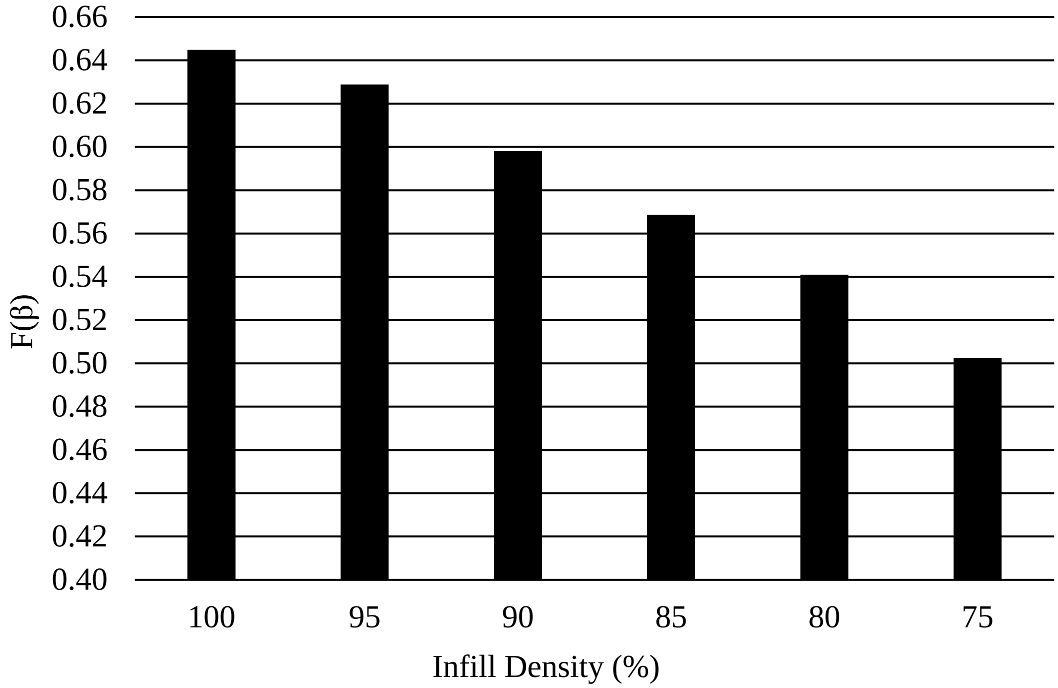

Figure 2- β-phase fraction in samples with different fill densities

Infill Pattern

Five different nozzle pathways were used to investigate the influence of infill pattern on the amount of β-phase within the printed samples. As it is concluded from Figure 3, although triangle and honeycomb had slightly higher amounts of crystalline β-phase than other patterns, the change in amount of this polymorph was minimal. Therefore, internal infill structures did not make a big change on the piezoelectric behavior of components.

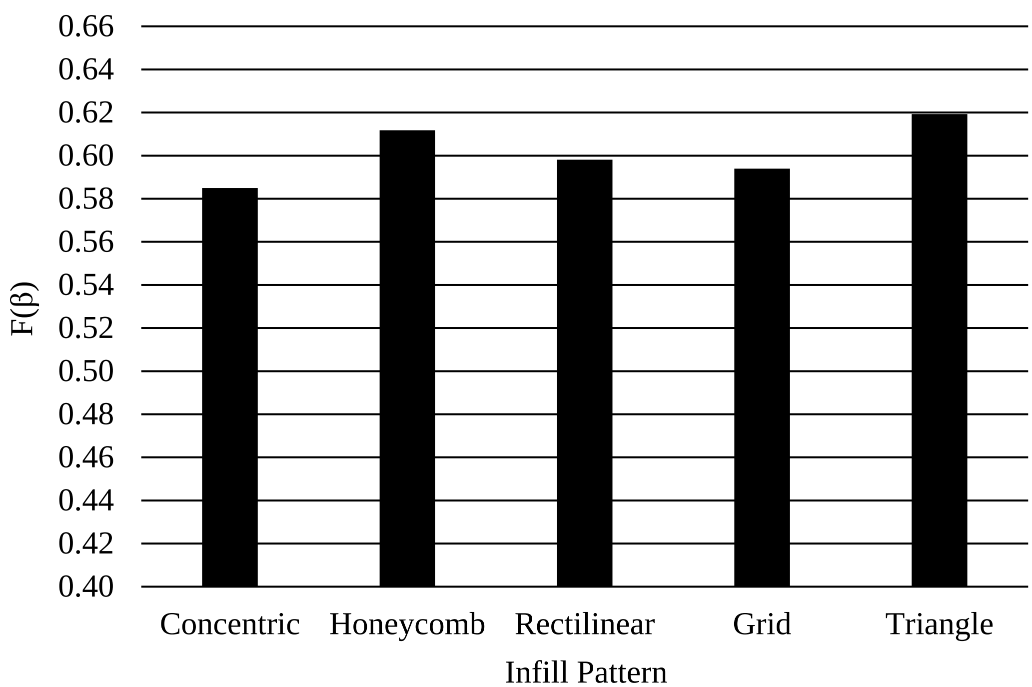

Figure 3- β-phase fraction in samples with different infill patterns

Layer Thickness

Since the layer thickness defines the number of cooling and heating cycles during deposition, it plays an important role in determining the residual stress state and distortion, which in turn affect the semi-crystalline microstructure development. Thinner layers are predicted to contain larger residual stresses compared to thicker layers, assuming the same thermal disparities between the deposited material and the underlying structure [20]. As shown in Figure 4, thinner layers have higher amount of crystalline β-phase than the thicker ones. As expected, in the specimens with 0.05mm thickness layers, warping (deformations relieving internal stresses) has occurred and this poor adhesion quality between the first printed layer and platform may affect the β-phase content, hence it had less β-phase fraction than the sample with 0.1 mm layers height.

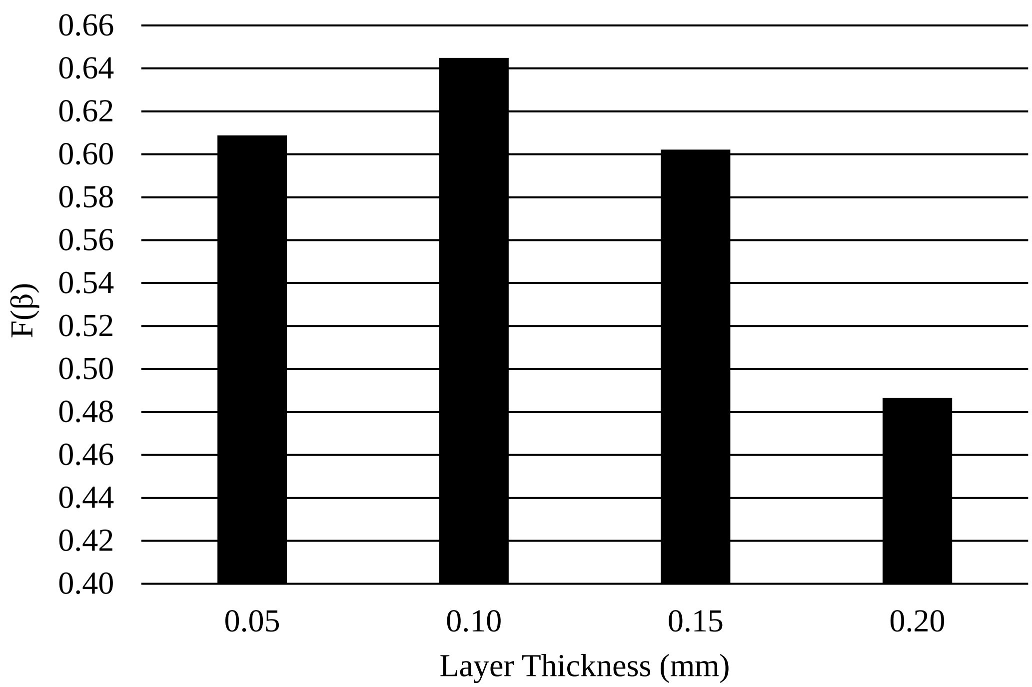

Figure 4- β-phase fraction in samples with different layer thicknesses

Nozzle Diameter

Nozzle diameter is another parameter that was found to have an effect on the amount of β-phase within the printed samples. Nozzle diameter determines the print resolution and affects the speed of printing. In this case, five different brass nozzles with sharp geometry were used to extrude PVDF filament. Figure 5 presents the relation between F(β) and nozzle diameter. According to this plot, the conical nozzles with 0.2 mm and 0.4 mm diameters have higher amount of β-phase fraction than the rest, and there is a drop off in the piezoelectric properties with bigger diameters (0.8mm and 1 mm) which was related to delamination occurred in these 3D parts.

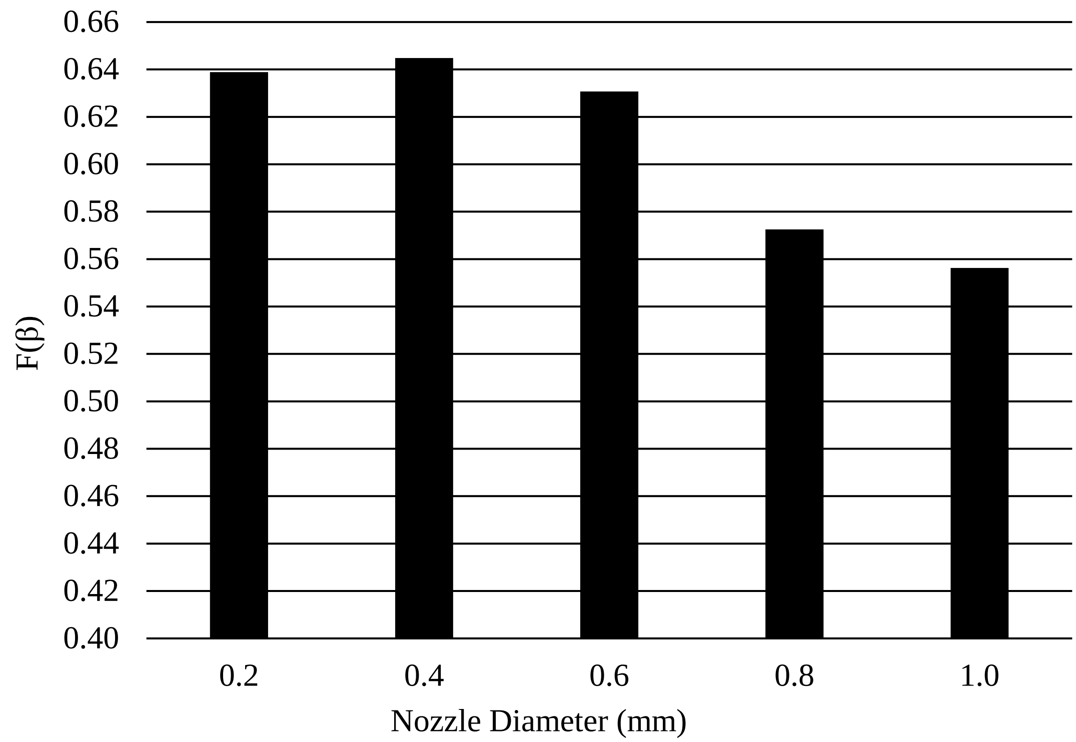

Figure 5- β-phase fraction in samples with different nozzle diameters

Summary and Conclusions

Infill density, layer thickness, and nozzle diameter were found to be the most influential parameters affecting the amount of β-phase content in fused filament fabrication PVDF components. The volume fraction of air gap has profound effect on the piezoelectric properties of the 3D printed parts, in which the part with 100% infill density has about 22% higher amount of fraction of β-phase than its counterpart with 75% infill density. Hence, the presence of voids or pores will gradually decrease piezoelectric properties of printed samples, which means that more dense parts have higher β-phase content. Layer thickness, which has a direct impact on warping and distortion issue, is another major factor that evaluated in this research. By increasing the layer thickness, F(ß) decreased. For instance, the fraction of β-phase content for samples with 0.1 mm and 0.2 mm layer height, was about 0.64 and 0.48, respectively. Another way to get higher piezoelectric properties in the additively manufactured parts is related to nozzle diameter, smaller diameter of conical nozzles produced PVDF samples with higher fraction of β-phase than larger ones. The infill pattern was not a significant influencing parameter on the PVDF microstructure. Although triangle and honeycomb had slightly higher amounts of crystalline β-phase than other geometries, the change in amount of this polymorph was minimal.

Acknowledgments

The Authors would like to acknowledge Luther B. Hutcherson in chemistry department at University of Louisville for his help to do FTIR characterization test for this research study.

References

1. Fukada, E., *History and recent progress in piezoelectric polymers.* IEEE Transactions on ultrasonics, ferroelectrics, and frequency control, 2000. **47**(6): p. 1277-1290.

2. Dineva, P., et al., *Piezoelectric Materials*, in *Dynamic Fracture of Piezoelectric Materials*. 2014, Springer. p. 7-32.
3. Li, H., C. Tian, and Z.D. Deng, *Energy harvesting from low frequency applications using piezoelectric materials.* Applied physics reviews, 2014. **1**(4): p. 041301.
4. Ruan, L., et al., *Properties and Applications of the β Phase Poly (vinylidene fluoride).* Polymers, 2018. **10**(3): p. 228.
5. Derakhshani, M., T. Berfield, and K.D. Murphy, *Dynamic Analysis of a Bi-stable Buckled Structure for Vibration Energy Harvester*, in *Dynamic Behavior of Materials, Volume 1*. 2018, Springer. p. 199-208.
6. Tuzzolino, A., *Applications of PVDF dust sensor systems in space.* Advances in Space Research, 1996. **17**(12): p. 123-132.
7. Gallantree, H., *Review of transducer applications of polyvinylidene fluoride.* IEE Proceedings I-Solid-State and Electron Devices, 1983. **130**(5): p. 219-224.
8. Wang, H., et al., *A robust superhydrophobic PVDF composite coating with wear/corrosion-resistance properties.* Applied Surface Science, 2015. **332**: p. 518-524.
9. André-Castagnet, S. and S. Tencé-Girault, *Relationships between mechanical tensile behavior and micro-mechanisms in poly (vinylidene fluoride) at high temperatures: Influence of the molecular weight distribution.* Journal of Macromolecular Science, Part B, 2002. **41**(4-6): p. 957-976.
10. Sencadas, V., R. Gregorio Jr, and S. Lanceros-Méndez, *α to β phase transformation and microestructural changes of PVDF films induced by uniaxial stretch.* Journal of Macromolecular Science®, 2009. **48**(3): p. 514-525.
11. Mohammadi, B., A.A. Yousefi, and S.M. Bellah, *Effect of tensile strain rate and elongation on crystalline structure and piezoelectric properties of PVDF thin films.* Polymer testing, 2007. **26**(1): p. 42-50.
12. Lee, C. and J.A. Tarbutton, *Electric poling-assisted additive manufacturing process for PVDF polymer-based piezoelectric device applications.* Smart Materials and Structures, 2014. **23**(9): p. 095044.
13. Tarbuttona, J., et al., *Phase transformation and shock sensor response of additively manufactured piezoelectric PVDF.* Procedia Manufacturing, 2017. **10**: p. 982-989.
14. Kim, H., et al., *Integrated 3D printing and corona poling process of PVDF piezoelectric films for pressure sensor application.* Smart Materials and Structures, 2017. **26**(8): p. 085027.
15. Porter, D.A., T.V. Hoang, and T.A. Berfield, *Effects of in-situ poling and process parameters on fused filament fabrication printed PVDF sheet mechanical and electrical properties.* Additive Manufacturing, 2017. **13**: p. 81-92.
16. Dunsch, R. and J.-M. Breguet, *Unified mechanical approach to piezoelectric bender modeling.* Sensors and Actuators A: physical, 2007. **134**(2): p. 436-446.
17. Momenzadeh, N., C.M. Stewart, and T. Berfield, *Mechanical and Thermal Characterization of Fused Filament Fabrication Polyvinylidene Fluoride (PVDF) Printed Composites*, in *Mechanics of Additive and Advanced Manufacturing, Volume 8*. 2019, Springer. p. 59-65.
18. Huan, Y., et al., *Influence of extrusion, stretching and poling on the structural and piezoelectric properties of poly (vinylidene fluoride-hexafluoropropylene) copolymer films.* Journal of applied polymer science, 2007. **104**(2): p. 858-862.
19. Salimi, A. and A. Yousefi, *Conformational changes and phase transformation mechanisms in PVDF solution-cast films.* Journal of Polymer Science Part B: Polymer Physics, 2004. **42**(18): p. 3487-3495.
20. D'Amico, A.A., A. Debaie, and A.M. Peterson, *Effect of layer thickness on irreversible thermal expansion and interlayer strength in fused deposition modeling.* Rapid Prototyping Journal, 2017. **23**(5): p. 943-953.