A Review on 3D printing of piezoelectric materials

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Abstract: This paper presents an overview of 3D Printing methods of Piezoelectric materials (PEM) using various poling techniques, such as corona poling, contact poling, and other poling process, the method of integrating the 3D printing and poling, enables to print any type of sophisticated shaped sensors in single step, several conventional methods require complicated and time-consuming procedures, the 3D printing integrated with poling possess method and material constraints, the steps to minimize the technical challenges are under research.

Keywords: 3D Printing, Piezoelectric material, corona poling, contact poling.

1. Introduction
The Additive manufacturing colloquially known as 3D printing enabled us to manufacture customized parts with complex shapes from polymers, ceramics and metals without the need for molds or machining typical for conventional formative and subtractive production. Grabbing the attention of people across the globe for various applications such as construction industries[1], medicine[2], food[3], aerospace[4], soft sensors and actuator applications[5].

The 3D printing of piezoelectric materials is done by several techniques depending upon the material type polymers, ceramics, polymercomposites, the 3D printing of piezoelectric materials is done in three methods, they are poled piezoelectric materials are 3D printed, poling during 3D printing this is also known as in-situ poling and poling after 3D printing of piezoelectric material. The piezoelectric materials have numerous applications such as military and marine applications[6], sensors[7], ultrasonic transducers[8, 9], nanogenerators[10], automotive industry, smartphones and other everyday applications[11].

2. Piezoelectric Materials
Piezoelectric materials are the noncentrosymmetric dielectric materials, when these materials experience an external strain by applying pressure/stress, electric field across the crystal is generated by creation of positive and negative charges on opposite faces in the crystal, due to the orientation of electric dipoles in the crystal, this is called as direct piezoelectric effect, this is observed by Jaques and Pierre curie in 1880[45]. The converse of this is when an external electric field is applied on the crystal, the asymmetric displacements of anions and cations creates a considerable net deformation of the crystal; the strain in piezoelectric materials is extensive or compressive, depending on the polarity of the applied field; this phenomenon is known as “indirect piezoelectric effect”, the indirect piezoelectric [46] is stated using fundamental thermodynamic principles, the constitute equations of direct and indirect piezoelectric effect are given below[47].
Direct effect: \[ D = dT + \varepsilon E \] ................................ (1)

Indirect effect: \[ X = sT + dE \] ............................... (2)

Where \( D \) = electrical displacement, \( d \) = piezoelectric coefficient, \( T \) = stress, \( \varepsilon \) = permittivity of the material, \( E \) = electric field, \( X \) = Strain, \( s \) = mechanical compliance.

Some of the piezoelectric materials exhibit spontaneous polarization that decreases with increasing temperature, and these are called as pyroelectric materials, in some of the pyroelectric materials, the spontaneous polarization can be reoriented by applying an electric field, and such materials are known as ferroelectric materials, subsequently the ferroelectric materials possess both pyroelectric and piezoelectric characteristics, this piezoelectric materials are in different structures, for example, crystalline or amorphous form, polymer form and mixture of this two materials are as polymer-ceramic form, this are explained as follows:

2.1 Ceramic materials

Piezoelectric materials can be natural or man-made. The natural PEM are crystal materials like quartz (SiO₂), Topaz, Rochelle salt, Tourmaline-group minerals and some organic substances as silk, bone, wood, enamel, hair, dentin, rubber. Man-made piezoelectric materials are crystals that are quartz analogs, ceramics, polymers and composites, There are the accompanying groups of man-made ceramics with crystal structure as perovskite: Barium titanate (BaTiO₃), Lead titanate (PbTiO₃), Lead zirconate titanate (Pb[ZrₓTi₁₋ₓ]O₃, 0 < x < 1) more commonly known as PZT, Potassium niobate (KNbO₃), Lithium tantalate (LiTaO₃), Lithium niobate (LiNbO₃), etc. and other lead-free piezoceramics. The general chemical formulae of perovskite crystal structure is ABO₃, where A is a larger metal ions, usually lead Pb or barium Ba, B is a smaller metal ion, usually titanium Ti or zirconium Zr.

Ceramic materials possess extensive electrical properties. Some of them restricted passage of an electric current even in a very strong electric field and consequently are excellent insulators. Others allow passage of an electric current and have application as electrical conductors. The third kind enables an electric current to pass only under specific conditions or when an energy threshold has been reached and thus are useful semiconductors. However, some ceramics do not conduct electricity but undergo internal charge polarization that allows the material to be utilized for storage of an electrical charge in capacitors. Examples of electro-ceramics include Zinc oxide for varistors, lead zirconium titanate (PZT) for piezoelectrics, barium titanate for capacitors, tin oxide as gas sensors, lead lanthanum zirconium titanate (PLZT) and lithium niobate for electro-optic devices.

2.2 Polymer

The generally known piezoelectric polymers are polyvinylidene fluoride (PVDF) and its copolymers, the molecular formula of PVDF is [C₂H₂F₂]ₙ, the PVDF polymer exists in three different phases: α, β, and γ phases. PVDF in β and γ phases are polar, while in α phase is nonpolar, for piezoelectric applications, thin films of PVDF in the highly polar β phase are used.

PVDF thin films are generated either from the melt or from solution[48, 49]. The phase of the film formed relies upon the method used for solidifying the melt or the type of solvent used, α and β phases are formed, when the melt (temperature > 167°C) is quenched to 80°C. The α phase PVDF film transforms to highly polar β phase, when α phase PVDF film is stretched to 300% strain. The α-phase PVDF film is usually utilized as insulating material because of its low thermal conductivity, low density, and high chemical and heat resistance[12]. PVDF is synthesized from solutions by using solvent cast method. The solvents used are dimethyl formamide or dimethyl acetamide. PVDF films
are poled under stretched condition by applying high electric field of the order of 20 kV/mm. The piezoelectric coefficient of PVDF film is in the range of 20–30 pC/N, which is ten times lower than that of PZT.

Copolymers of PVDF with trifluoroethylene and tetrafluoroethylene display better piezoelectric properties over pure PVDF. The piezoelectric coefficient of the copolymer P(VDF-TrFE) is greater than 100 pC/N. The most extreme working temperature for the β-phase PVDF film is 80°C and 110°C for the β-phase PVDF-TrFE film[12]. This polymers are used as presser sensors rather than actuators because of their low stiffness constant. The polymers are more suited for manufacturing of hydrophones (underwater sonar detectors) than PZT because of their excellent impedance matching with water. Other typical applications include pressure sensors in diesel injection lines and shock wave sensors.

2.3. Ceramic polymer

Ceramic polymer-based composites are formed by combining properties of at least two materials relying upon the applications; they are used widely in various industrial applications that range from sensors and actuators to embedded electronics[13], for these purposes, composites of 0-3 connectivity, which implies that a three-dimensionally associated polymer phase is loaded with isolated ceramic particles, have gained interest particularly to enable freedom of design in flexible form as well as inexpensive posses[14]. Nanocomposites integrating piezoelectric ceramic fillers within a polymer matrix have attracted considerable interest due to a unique combination of piezoelectric properties and polymer matrix flexibility.

The enhancement of properties observed in piezo-polymer composites[15] is because the properties of the constituent phases combine to increase the mechanical properties and range of applicability of the composite. The efficient piezoelectric and dielectric properties of two-phase composites are not comparable to their single phased counterparts because of the polymer matrix, which has lower dielectric constants and piezoelectric coefficients in comparison to the embedded piezoelectric ceramic. Hence, several researchers have demonstrated that the incorporation of electrically conductive particles within the polymer matrix will enhance the polarization of the embedded piezoelectric fillers within the matrix, thereby enhancing their electrical properties[16]. Recently, carbon nanotubes (CNTs) have emerged as appealing fillers[16] due to their electrically conductive nature[17]. However, less is known about the interrelationship between the composite processing technique, morphology and properties of the electrically conductive particles, which dictate the piezoelectric and dielectric properties of the materials. The successfully 3d printed ceramic-polymer piezoelectric composite are BaTiO3– PVDF[18], BaTiO3–PEGDA[19].

3. Poling

Poling is the orientation of the microscopic molecular dipoles along the field direction by applying external electric field, this aligning process is discovered by Gray et al [50], it is a procedure that initiates piezoelectricity in ferroelectric ceramics by applying an electric field to switch the polar axis of crystallites to the symmetry-allowed directions nearest to the applied field [20]. Poling will convert inert ceramics into electromechanically active materials[21]. Poling is an essential step in obtaining the desired piezoelectric properties of the material. In composites that are polymer based poling is carried out at its glass transition temperature, by gradually heating it and by placing it in a strong static external electric field[22, 23]. The temperature at which poling takes place and the applied field strength are critical parameters in characterizing the electromechanical properties of the poled material. Both the temperature and the applied field are required to decrease the energy band gap to orient the
domains in the direction of the field, orientation process and the chosen poling temperature depend on the internal order of the polymer electrets, i.e., if it is semicrystalline or amorphous.

For some materials like PVDF, mechanical stretching of the polymer film during the poling process increases the quality of the crystallite alignment. Stretching the polymer essentially aligns the amorphous chains in the film plane and facilitates uniform rotation of the crystallites by an electrical field. Depending on whether stretching is uniaxial or biaxial, the electrical and mechanical properties (and therefore the transduction response), are either highly anisotropic or isotropic in the plane of the polymer sheet. For semicrystalline polymers, the amorphous phase bolsters the crystal orientation, and the polarization is stable up to the Curie temperature ($T_C$). Most multiphasic composites have been traditionally poled using the contact poling method. In this poling method, the material is in direct contact with the poling electrode/needle. However, there are some disadvantages of this technique as it can cause dielectric breakdown of the composite material, especially when the composite has conductive inclusions[22, 23]. Also in this method, the samples are required to place inside a silicone oil bath for uniform heating of the sample. To overcome the challenges of this method, researchers[20] have developed the corona discharge poling method, in this method high poling voltage is applied to air molecules above sample, thereby eliminating physical contact. Researchers have also demonstrated that higher voltages can be accomplished by the corona poling method in comparison to traditional contact poling method [23, 24].

3.1 Corona Poling

In the corona poling technique, charge from the corona point/needle is sprayed onto the surface that has no electrode, creating an electric field between the sample surfaces. As a result of the absence of electrodes, there is no shorting of the sample at weak spots, further higher poling voltages can be achieved. This method additionally enables samples of larger area to be poled and might be adapted to a continuous process for mass production. Here the live wire is connected to the corona discharge needle, and the base plate upon which the sample is rests is grounded as shown in Figure 1. The fine tip of the corona needle ensures that adjacent air molecules are ionized. The whole poling setup is placed inside a protective casing. This ensures that the ionized air molecules do not make contact with surrounding objects. The separation between the needle and sample is a critical experiment variant and studies have demonstrated that different distances can influence the poling procedure significantly [20]. So for these experiments, the corona needle distance from the sample was kept constant at 10 mm to ensure experiment repeatability and eliminate experiment variability.

![Figure 1. Corona discharge technique, the live wire ionizes the surrounding air molecules onto the sample surface without the electrode. There is no physical contact between the corona needle and the surface of the sample.](image)
3.1.1. Electric Poling assisted Additive Manufacturing (EPAM)

Electric Poling assisted Additive Manufacturing (EPAM) [25, 26] is a poling during printing method by using corona poling process, this method combines Additive Manufacturing (AM) and electric poling processes and can construct free-form shape piezoelectric devices continuously. In this procedure, the PVDF polymer dipoles remain uniform and well aligned over a large area in a single design, synthesis, and fabrication step. In the EPAM process, under high electric field and higher temperature, the molten PVDF polymer is electrically poled and in parallel mechanically stressed in-suit by the leading nozzle. The EPAM system is used to fabricate piezoelectric devices by applying high electric field between nozzle tip and printing bed in AM machine, to directly print piezoelectric structures from PVDF polymeric filament.

In this process, PVDF polymer devices with 100 mm long, are printed under four various circumstances of the electric field: 0.0 MV m$^{-1}$, 1.0 MV m$^{-1}$, 2.0 MV m$^{-1}$, and 3.0 MV m$^{-1}$. 0.3 mm is the printing gap between printing to surface and nozzle tip. Burning in the initial printing layer is occurred during poling and an electrical breakdown occurred at 3.0 MV m$^{-1}$ electric field this remained as a challenging task in maintaining a constant electric field, this leads to the operating limitation of the below setup up to 3.0 MV m$^{-1}$ Figure 2.(e). High electric field causes sharper peaks at the polar β crystalline wavenumber of the PVDF polymer. The results show that α phase is transformed to β phase of PVDF polymer due to molecular chain alignment and dipole alignment by applying a strong electric field while printing simultaneously.[25, 26]

![Piezoelectric PVDF printing system.](image)

**Figure 2.** Piezoelectric PVDF printing system. (a) Schematic diagram of electric poling-assisted additive manufacturing (EPAM) process, (b) experimental setup combined additive manufacturing process and electric poling process, (c) experimental results of electric poling and mechanical stretching process in EPAM process, (d) extrusion result of filament type of PVDF polymer. PVDF polymer feeds into extruder under 230 °C, and its feed is controlled by an extruding motor, (e) Printing surface damage due to the corona discharge, (f) Burning spot [25, 26].

3.1.2. Integrated 3D Printing and Corona poling (IPC)

Integrated 3D Printing and Corona poling (IPC)[51] is a poling during printing method, is also stated as in-situ poling during 3D printing process, incorporated 3D printing process with corona poling empowered to manufacture piezoelectric PVDF sensors without post poling process. In this process...
poling is performed in regulated heating environment by applying high electric field using nozzle as anode and heating bed as cathode. The nozzle passes along the programmed path by a fixed distance between nozzle tip and sample’s top surface. In parallel electric field between the nozzle and bottom heating pad advances the arrangement of dipole moment of PVDF molecular chains. IPC is an enhanced EPAM process that applies a higher electric field during 3D printing. It was found that applying more than 2 MVm\(^{-1}\) may cause electric breakdown which emits a transient electromagnetic disturbance that could cause the printer to lose communication with the computer. Another limitation of the EPAM technique utilized was limited to create only a single layer of a piezoelectric device. Therefore, the EPAM process was modified to enable the application of a higher electric field (40 MVm\(^{-1}\)) and print multiple layers as shown in Figure 3.

Figure 3. Schematic of IPC process setup: (a) 3D printing of PVDF layer, (b) Corona poling process[51].

The 0.9 mm of gap is maintained in between the nozzle and bed to avoid the nozzle touching the sample with out blocking the printing of initial layer and to maintain enough distance for applying high electric voltage. The operating temperature is 230 °C to 260 °C and printing speed is less than 10 mm s\(^{-1}\) with the limitation of minimum 1 mm s\(^{-1}\) by 3D printer software. 12 kV (13.3 MV m\(^{-1}\) = 12 kV/0.9 mm) is the maximum working electric voltage without hindering the printing process. The user operating the 3D printer during the IPC process is cautioned to maintain distance as part of safety measures involving in operating high voltage applications. In the IPC technique, it was observed that increasing the heating bed temperature reduces the piezoelectricity of the PVDF film[51] and in this process piezoelectric output current up to ±0.106 nA is generated by applying 12 kV electric voltage.

3.2 Contact poling

This is the conventional poling technique, in which piezoelectric ceramics and composites are poled by applying a large dc voltage. This poling method requires physical contact of the live electrode with the sample electrode and with the application of a very large electric field the sample will be poled. However, application of large dc fields to polymer matrix composites often cause dielectric breakdown of the sample. The samples are placed in a silicone oil bath and uniformly heated throughout up to its glass transition temperature as shown in Figure 4. The samples need to be coated with a top electrode for this method in addition to a bottom electrode and poling is usually limited to samples of smaller area[20].

The advantage of this poling configuration depends on the homogeneity and the direct control of the poling field. The electrode poling, is simpler than the corona poling. Contact poling has different experimental setups, they are contact poling at room temperature, contact poling with a cycle of temperature (thermal poling) or the Bauer cyclic poling method[27-31]. Depending on your needs you can choose one or another. One of the major drawbacks of this method in addition to the dielectric breakdown is the local breakdown at weak spots, such as pinholes, short-circuits of the electrodes and
prevents further poling. This is reason of performing the poling process in a vacuum chamber or immersed inside an electrically insulating fluid [32, 33]. Moreover, it can be limited by charge injection processes near sharp electrode edges or internal voids, so a protective design of electrodes shape is necessary. In order to improve this form of poling the corona discharge technique was developed [20].

Figure 4. Contact poling setup for electrically aligning samples. The poling electrode is in contact with the sample top electrode. The base plate on which the sample rests is grounded.

3.2.1 3D Optical Printing of Piezoelectric Nanoparticle.

3D Optical Printing of Piezoelectric Nanoparticle [19] is a technique uses contact poling post process of printing, this is the poling after printing method, in this technique the polymer composite materials are optically printed into three-dimensional (3D) microstructures using digital projection printing, in this process piezoelectric polymers are synthesized by mixing barium titanate (BaTiO₃, BTO) nanoparticles with photoliable polymer solutions such as polyethylene glycol diacrylate and exposing to digital optical masks that could be dynamically altered to generate userdefined 3D microstructures. To increase the mechanical-to-electrical conversion efficiency of the composites, the BTO nanoparticles are chemically modified with acrylic surface groups, which formed direct covalent linkages with the polymer matrix under light exposure. The piezoelectric coefficients ($d_{33}$) of $\sim 40$ pC/N is observed by 10% mass loading of the chemically modified BTO nanoparticles and this is more than 10 times larger than composites synthesized with unmodified BTO nanoparticles and over 2 times larger than composites containing unmodified BTO nanoparticles and carbon nanotubes to boost mechanical stress transfer efficiencies. These results helps to fabricate efficient 3D piezoelectric polymers by nanointerfacial tuning.

Figure 5. (a) Schematic of the digital projection Printing (DPP) setup that projects dynamic digital masks on the photoliable piezoelectric nanoparticle-polymer composite solution. Any pattern can be digitized, and the digital mirror device projects the image onto the polymer solution, (b) Scanning electron micrograph of BTO nanoparticles grown via a hydrothermal process, (c) Cartoon showing the piezoelectric polymer composite materials with BTO nanoparticles (orange circles) grafted to a
PEGDA matrix (black lines). The zoom-in shows the TMSPM linker covalently linked to the nanoparticle surface and cross-linked with the PEGDA matrix[19].

Figure 6. Collage of piezoelectric microstructures printed using DPP including (a) a dot array, (b, c) square arrays with different sized void spaces, and (d) a honeycomb array. All structures were fabricated in <2 s using a PEGDA solution loaded with 1% of the TMSPM-modified BTO nanoparticles, (e) a mushroom-like array, (f) a cross array, and (g) a tapered cantilever array (dark region, cantilever; light region, support). (h) Microtubule structure created by releasing a honeycomb array from the substrate. The film rolls up after release due to slight stress gradients in the film [19].

After photofabricating the composite materials, the printing cell can be used to activate the polymer. This requires that the dipoles in the perovskite crystallites be aligned using a poling field that is larger than the coercive field (∼10 V/μm) of the BTO nanoparticles. This was achieved using indium tin oxide (ITO)-coated glass slides as the top and bottom electrodes, which also served as the top and bottom surface of the photofabrication cell. By placing an elastomeric spacer (e.g., PDMS or Kapton film) between the conductive glass substrates, the maximum height of the photofabricated structures is defined, and precise electric fields could be applied to polarize the BTO nanoparticles. After activating the piezoelectric composite, the fabricated films can be either left on the glass slides for testing and characterization, removed to create freestanding structures, or transferred to other substrates for further integration[19].

3.3 One-Step Solvent evaporation-assisted 3D Printing of Piezoelectric PVDF NanoComposite.

One-Step Solvent evaporation-assisted 3D Printing of Piezoelectric PVDF NanoCompositestructures[34] is the poling before printing method, however there is no poling involved in this process, due to inherent piezoelectric β-phase of PVDF is used which is already poled, so this process is considered as poling before printing method. In this technique β-phase PVDF and barium titanate are used to fabricate self-supporting piezoelectric structures on a micro- to millimetre scale by solvent evaporation-assisted 3D printing at room temperature. In this process the dissolution of the nanocomposite into a highly volatile solvent followed by extrusion through a small nozzle under applied pressure [35, 36]. The rapid evaporation of the solvent results in retention of the desired shapes: layer-by-layer, self-supporting, and even freestanding structures [35]. The application of this work is highlighted in the form of a ready-to-use millimetre scale 3D contact sensor fabricated in a single printing step.
Figure 7. (a) Solvent evaporation-assisted 3D printing process for PVDF nanocomposite-based 3D structures. (b) Photograph of the 3D cylindrical sensor during a finger-tap test. (c) Piezoelectric voltage output of the 3D cylindrical sensor upon five consecutive finger taps. (d) Schematic of the proposed process leading to increase in $\beta$-phase fraction in PVDF due to filler addition[34].

In Figure 7.d Ball-milling mechanically activates the BaTiO$_3$ NPs (BT), which provides adhesion sites for PVDF chains. The polymer chains crystallize into aligned $\beta$-phase upon extrusion through the nozzle. The NP agglomerates arrest the PVDF chains in the $\beta$-phase upon solidification, thus leading to improved piezoelectric properties.

A 3D contact sensor that generates up to 4 V upon gentle finger taps demonstrates the efficacy of the fabrication technique. This one-step 3D printing of piezoelectric nanocomposites can form ready to use, complex-shaped, flexible, and lightweight piezoelectric devices. When combined with other 3D printable materials, they could serve as stand-alone or embedded sensors in aerospace, biomedicine, and robotic applications.

3.4 All-Polymer-based piezoelectric photocurable resin for 3d Printing

All-Polymer-based piezoelectric photocurable resin for 3d Printing[37] is the poling after printing method, this technique developed an all-polymer-based piezoelectric photocurable resin (V-Ink) suitable for additive manufacturing processes based on light-controlled polymerization techniques. By taking into account the trade off between the manufacturability and piezoelectric characteristics, the optimized V-Ink contains 35 wt.% of polyvinylidene fluoride (PVDF) particles being suspended in the photocurable resin. This process demonstrates a 3D printed piezoelectrically-active thickfilm with an optimized piezoelectric voltage coefficient ($g_{33}$) of $105.12 \times 10^{-3}$ V·m/N. This new materials will bring promising opportunities for additive manufacturing of flexible functional devices, especially for novel applications in bio sensing and detection.
Figure 8. (a) Schematic illustration of the PμSL system and the 3D printing process flow shown from (b) – (g).[37]

Figure 9. (a) 3D printed PVDF layer for piezoelectric sensor; (b) Schematic illustration of the poling setup of the PVDF thin film with Al electrodes; (c) Schematic illustration of setup measuring the output voltage when the PVDF thin film with electrodes is subjected to applied force [37].

This process is done in 3 steps, in the first step is to make the V-Ink manufactural for 3D-printed piezoelectric devices, the PVDF particles are required to be uniformly dispersed within the V-Ink during the fabrication process, in the second step long waiting time is necessary in dealing with high-viscosity resin during the recoating step. Therefore, the viscosity of the resin needs to be optimized to control the dwell time but without compromising the fabrication throughput. In the third step is to optimize the piezoelectric performance of the V-Ink, the resin’s piezoelectric characteristics dependent on the concentration of PVDF and poling electric field is evaluated experimentally on the premise of manufacturability of the V-Ink[37].

In the future, to achieve optimal manufacturability, piezoelectric characteristics, and mechanical properties, quantitative methods will be employed to optimize the concentration of V-Ink’s different components including diethylfumarate (DEF) as solvent, 1,6-hexanediol diacrylate monomer (HDDA) and PVDF. Additional work will be explored to further increase the manufacturability and piezoelectric performance of the V-Ink. For example, heating can be integrated with the 3D printing process as heating can reduce the effective viscosity of the V-Ink[52], thus making it possible to print V-Ink with high concentration of PVDF. In addition, the introduction of micro-continuous liquid interface production system allows more flexibility as the fabrication speed is much faster than PμSL[53], thus the PVDF can be completely dispersed during the whole fabrication process. Moreover, the mechanical properties of the printed devices, including tensile/bending properties, will be characterized and optimized for the application in flexible functional devices. This work represents an initial point in the development of an effective all-polymer based piezoelectric photo curable resin for 3D printing techniques, and opens up new opportunities for functional devices, especially the devices for biomedical sensing, to be rapidly produced at low cost using emerging 3D printing techniques.

3.5 3D Printing of Piezo nanocomposite and Thermal Poling

In this technique BaTiO3/ PVDF composite is 3D Printed followed by Thermal poling [18], this process comes under poling after printing method. In this process 9 wt.-% BTO/PVDF sheets were fabricated by using solvent-casting, the sheet was cleaved into several 5 cm². The cleaved samples were then fed to a filament extruder (Filabot) at a temperature of 200°C. Filament with diameter 2.7 mm is extruded and spooled, fabricated BTO/PVDF nanocomposites filament was then placed in to FDM 3D printer, also known as an extrusion-based process, which deposits materials in the form of a continuous flowing layer by layer to build a 3D structure [55]. Here an FDM 3D printing machine (Lulzbot Taz 5) was used to fabricate thin films of 0.33 mm in thickness with dimensions of 11.5x37 mm at a nozzle temperature of 250°C, the printing speed was set at 5 mm/s, and the heating bed temperature at 80°C. It is important to note that BTO may burn and clog the nozzle when printing at
such high temperature. This issue is addressed by limiting the amount of time the filament remains within the heated nozzle.

![Figure 10](image)

**Figure 10.** Schematic diagram of (a) the experimental setup for piezoelectric output current measurement and (b) sample and electrode design[18].

After fabricating the two films by solvent-casting and 3D printing processes, the samples were then prepared for a thermal poling process, where extensive research has indicated the transformation of PVDF β-phase[38]. Copper paint electrodes were attached on samples, connected to a high voltage source, and exposed with high electric field of 35 MV/m, which was found to be maximum electric field before experiencing electric breakdown, a schematic of the set-up is shown in Figure 11 (b). A key point to consider is that PVDF requires at least 50 MV/m to be polarized due to high coercive electric field; however, BTO requires only about 35 KV/m [39, 40]. Electric breakdown was avoided by dipping samples into silicon oil at 90℃ which also helps accelerating polarization during the process. Thermal poling was performed for 2 h on both 3D printed and solvent-casted films[18].

The piezoelectric responses show higher current output in 3D printed film than solvent-cast one due to the homogeneous dispersion and alleviation of agglomeration for BTO particles as well as removing porosities and cracks resulted from the filament extrusion and 3D printing process. The 3D printing technique not only improves the piezoelectric property, but also provides freedom of design to fabricate different shapes of form of active nanocomposites[18].

3.6 3D Printing of Piezoelectric element for energy focusing and ultrasonic sensing

3D Printing of piezoelectric element for energy focusing and ultrasonic sensing[41] is a poling after 3d printing method, in this process apiezoelectric-compositeslurrywithBaTiO₃ nanoparticles (100nm)canbe3DprintedusingMask-Image-Projection-basedStereolithography (MIP-SL)technology. Afterapost-process,thedensityof5.64g/cm³wasobtained,whichcorrespondsto93.7%ofthedensity of bulkBaTiO₃ (6.02 g/cm³).Theprintedceramicexhibitsapiezoelectricconstantandrelativepermittivity of160pCN⁻¹ and 1350 respectively. Anultrasonictransducerwithprintingfocused piezoelectric element wasfabricatedtorealizethe energyfocusingandultrasonicsensing.A6.28MHzultrasoundscan wasachievedbythetransducerandsuccessfullyvisualizedthestructureofaporcineeyeball.
Figure 11. (a) Illustration of the MIP SL system. (b) Imaging pattern controlled by the projection. (c) 3D geometry designed by Solid Work. (d) Interface to control motor and projector. (e) Optical images of Green-part fabricated by MIP-SL system. (f) The 6.28-MHz ultrasonic scan through porcine eyeball using the printing focused transducer. (g) Ultrasonic imaging of porcine eyeball.[41]

A set of cylindrical piezoelectric samples (diameter 10mm, thickness 390 mm) were fabricated using MIP SL system, the poling field is 30 kV/cm at 100 °C for 30 min. For typical BaTiO₃, the dielectric loss (tanδ) is usually less than 0.1 and the remnant polarizations P_r is larger than 2μC/cm². The low dielectric loss of the printed ceramics (tanδ = 0.018) indicates that when working in a piezoelectric device, the energy loss of this sample is low. The printed piezoelectric components display piezoelectric properties that can be used in biomedical imaging and other applications[41].

3.7 3D Printing of PVDF with Near-field electrospinning (NFES)

3D Printing of PVDF with Near-field electrospinning (NFES)[42] is the poling while printing method, in this technique the wavy-substrate self-powered sensors (WSS) are produced in a direct-write and in-situ poled manner by 3D printed topologically tailored substrate. The manufacturing steps consist of additive manufacture of 3D printed flexible and sinusoidal wavy substrate, metallization and NFSElectrospun fibres in the 3D topology. This 3D architecture can considerably increase the piezoelectric output and useful to fabricate self-powered sensors for measuring foot pressure, finger-induced power generation and monitoring human motion. The suggested method presents the improvement of existing electrospinning technologies, which is the traditional method used for synthesizing nanofibers from the Taylor cones of premixed solution through electrically driving the polymeric jet in fabricating 3D structures and other reliable applications for biomedical and wearable electronics. The various materials such as polymers, composites and ceramics having diameter from microns to nanometers. The unavoidable restrictions with traditional electrospinning method is by morphological and geometric control[56].

Figure 12. (a) Diagram of the near-field electrospinning technique to fabricate direct-write PVDF fibres on top of wavy substrate. (b) Mechanical adhesion of wavy substrate with Cu foil as conductive
electrode. (c) Electrospun PVDF fibers on top of Cu-adhesive wavy substrate via NFES. (d) Fully encapsulation with PDMS (bottom inset: optical photo and SEM image of PVDF fibers deposited on top of wavy substrate, exhibiting the wavy and 3D topology). Scale bar is 200 μm[42].

Figure 13. (a) The demonstration of WSS integrated self-powered foot pressure sensor arrays (3×3; 4.5 cm×3 cm of dimension for each unit cell) for detecting the foot pressure (inset: visually illustrated insole on top of the foot pressure sensor device). (b) and (c) shows two dimensional contour plot mapping of pressure potential from the objects of (b) normal foot, (c) flat foot. (d) In a tip-toed position and the related two dimensional contours plot mapping of pressure potential[42].

Figure 13 presents the four steps of fabrication of piezoelectric generator with fibres of wavy and three-dimensional (3D) topology. In the first step Cu foil is mechanically stuck to the thermoplastic elastomer (TPE) substrate with 3D printed wavy surface (Figure. 13a, TPE substrate thickness is around 2 mm). Figure 13 b depicts adhesively bonded wavy substrate and the PVDF piezoelectric fibres are continuously deposited on the Cu foil electrode through in-situ poled NFES technique (Figure. 13c, NFES processing setup is the followings: needle top to Cu collector distance ~1.5 mm, the electrospinning process parameters used in this case are 16 wt% PVDF, solvent (Dimethylformamide DMF: acetone with 1:1 weight ratio), 4wt% fluoro-surfactant (Capstone FS-66)). NFES has the great controllability to deposit very delicate pattern of fibers into the substrate. In the final step PDMS is used to isolate and encapsulate from the environmental disturbances[42].

The novelty of this technique is to present the topologically 3D wavy structures with increased piezoelectric and electrical properties. The above 3D architecture is capable of increasing the piezoelectric output and reasons might be mainly due to longest fibre length as electrospun by NFES process. Following by, the site addressable capability of piezoelectrically integrated 3D architecture is directly applied to the wearable device and smart button applications such that the button-hitting operation can be functionally discernable to any specific remote control features in a self-powered manner. The above demonstrated method is capable to advance the existing electrospinning technologies in constructing 3D structures for wearable electronics and biomedical applications[42].

Table 1. Summary of 3D Printing Methods.

| 3D Printing technique                  | Poling method                  | Material successfully printed | Operating conditions          |
|---------------------------------------|--------------------------------|-------------------------------|-------------------------------|
| Electric Poling assisted Additive Manufacturing (EPAM), (2014)[26]. | Corona poling during printing method | PVDF polymer filament (Ø3.0 mm) | Extruder Temp -230°C Bed Temp -100°C Extruder feed- 200 (mm min⁻¹) Electric field -0.0/1.0/2.0/3.0 (MVm⁻¹) |
| Integrated 3D Printing                | Corona poling                  | PVDF polymer filament          | Nozzle Temp-230°C             |
and Corona poling (IPC), (2017)[43].

### 3D Optical Printing of Piezoelectric Nanoparticle, (2014)[19].

| Method | Poling before printing method | Barium titnate (BaTiO₃) nano particles incorporated in polyethylene glycol diacrylate photoliable polymer. | Electric field- 12MV/m
|---|---|---|---
| | Bed Temp - 23/60/100/140°C
| | Applied Voltage- 3/6/9/12 kV
| | Operating temperature -120°C

### One-Step Solvent evaporation-assisted 3D Printing of Piezoelectric PVDF Nano Composite (2017)[34].

| Method | Poling before printing method | Inherent piezoelectric β-phase PVDF and barium titanate mixed with volatile solvent. | Nozzle diameter = 100 μm
|---|---|---|---
| | Speed = 0.5 mm s⁻¹
| | Printing time = 120 s

### All-Polymer-based piezoelectric photocurable resin for 3d Printing (2016)[37].

| Method | Poling after printing method | Piezoelectric photocurable resin (V-ink) containing 35 wt% of PVDF | UV light-405 nm
|---|---|---|---
| | Electric field -1.33 (MVm⁻¹)

### 3D Printing of Piezo nanocomposite and Thermal poling (2017)[44].

| Method | Poling after printing method | 9wt.-%-BTO/PVDF filament (Ø2.7 mm) | Extruder Temp - 220°C
|---|---|---|---
| | Bed Temp - 80°C
| | Electric field -35 (MVm⁻¹)

### 3D Printing of Piezoelectric element for energy focusing and ultrasonic sensing (2016)[41].

| Method | Poling after printing method | Barium titanate (BaTiO₃) nano particles mixed with Triton x-100 dispersant. | Electric field 10/20/30 (kV/cm)
|---|---|---|---
| | Extruder Temp - 220°C
| | Bed Temp - 80°C
| | Operating temperature -122°C

### 3D Printing of PVDF with Near-field electrospinning (NFES), (2016)[42].

| Method | Poling while printing method | Encapsulation of PVDF fibers on top with PDMS and on bottom with Cu-adhesive wavy substrate. | Out put voltage 1V/1.5V/2V
|---|---|---|---
| | Out put current 50nA/80nA/110nA

### 4. Mathematical models of the charge Piezoelectric constant

The piezoelectric nanocomposite enables to manufacture flexible sensitive Microelectromechanical systems (MEMS) for various industrial applications, the piezoelectric properties of polymer–ceramic composites are predicted by Furukawa Model and Yamada model as follows:

#### 4.1 Furukawa Model

Furukawa studied a two phase system composed of spherical inclusion (i.e. ceramic filler) embedded in a polymer matrix, which in turn is covered with a homogeneous medium whose properties approximate the average composite properties. Furukawa formulated following equations for the dielectric and piezoelectric coefficients of 0-3 composites [57].

\[
\varepsilon_c = \frac{\varepsilon_m + 2\varepsilon_f}{1 - \varepsilon_f / \varepsilon_m} \quad (3)
\]

\[
d_{33,c} = \frac{\varepsilon_m}{15\varepsilon_f} \left[ \frac{2 + 3\varepsilon_f}{1 - \varepsilon_f} \right] d_{33,f} \quad (4)
\]

\[
g_{33,c} = \frac{15\varepsilon_f}{(1 + 2\varepsilon_f)(2 + 3\varepsilon_f)} g_{33,f} \quad (5)
\]
Where $V_f$ is the volume fraction of ceramic filler, $d_{33}$ and $g_{33}$ are piezoelectric charge constant and voltage constants respectively and $\varepsilon$ is the dielectric constant with the subscripts $f$ and $m$ corresponding to that of ceramic and polymer phase respectively ($\varepsilon_f >> \varepsilon_m$). The main drawback of Furukawa model is that no interactions between the constituent phases are taken into consideration while formulating the equations since the model consider the composite is electrically homogeneous. But this may not be true in case of a two-phase composite system due to the space charge effects (i.e. Maxwell-Wagner effect)[15].

### 4.2 Yamada model

Yamada examined the binary system consisting of PZT powder mixed with PVDF polymer and proposed a model to state the behaviour of the properties of the composite using the properties of its constituent materials. The model consists of ellipsoidal particles dispersed in a continuous polymer medium and the permittivity ($\varepsilon_c$) and piezoelectric charge coefficient ($d_{33,c}$) of the composite was given as follows[45, 46].

$$\varepsilon_c = \frac{1 + 2V_f}{1 - V_f} \left( 1 + \frac{nV_f \varepsilon_f - \varepsilon_m}{\varepsilon_m + \varepsilon_f - \varepsilon_m - 1 - V_f} \right) \quad \ldots \quad (6)$$

$$d_{33,c} = \frac{\varepsilon_f \gamma m \varepsilon_c (d_{33,f})}{n \varepsilon_c + \varepsilon_f - \varepsilon_c} \quad \ldots \quad (7)$$

where $n$ is the shape factor (depends on the geometry of the filler particles and its orientation with respect to the surface of the composite), $\gamma$ is the ceramic poling ratio, $V_f$ is the volume fraction of the filler particles and $\varepsilon$ is the dielectric constant with the subscripts $c, f$ and $m$ corresponding to the properties of composite, ceramic filler and polymer matrix.

### 5. Conclusion

The 3D printing of piezoelectric materials is performed in three methods, first method is poling before printing, second method is poling while printing, this is also known as in-situ poling and third method is poling after printing method, the most of this three methods uses contact poling or corona poling as per their material and designed technique to pole the material, the 3D printing of ceramic polymer nanocomposite provides the flexibility due to polymer portion and more piezoelectric properties due to piezoelectric nano ceramic particles, this piezoelectric properties are measured by piezoelectric charge coefficient ($d_{33}$) this is calculated by Furukawa model and Yamada model, Yamada model provides the more promising results over the Furukawa model due to consideration of interaction of the ceramic particle and polymer by using factor $(n)$, which relates the shape and relative orientation of the filler.

### Reference list

1. Tay, Y.W.D., et al., 3D printing trends in building and construction industry: a review. Virtual and Physical Prototyping, 2017. 12(3): p. 261-276.
2. Liaw, C.Y. and M. Guvendiren, Current and emerging applications of 3D printing in medicine. Biofabrication, 2017. 9(2): p. 024102.
3. Sun, J., et al., An Overview of 3D Printing Technologies for Food Fabrication. Food and Bioprocess Technology, 2015. 8(8): p. 1605-1615.
4. Wong, J.Y., 3D Printing Applications for Space Missions. Aerosp Med Hum Perform, 2016. 87(6): p. 580-2.
5. Valentine, A.D., et al., Hybrid 3D Printing of Soft Electronics. Adv Mater, 2017. 29(40).
6. Cross, L.E. and W. Heywang, Piezoelectricity Evolution and Future of a Technology Introduction. Piezoelectricity: Evolution and Future of a Technology, 2008. 114: p. 1-5.
7. Zhou, J., et al., Flexible piezotronic strain sensor. Nano Letters, 2008. 8(9): p. 3035-3040.
8. Zhang, S., et al., Advantages and Challenges of Relaxor-PbTiO3 Ferroelectric Crystals for Electroacoustic Transducers- A Review. Prog Mater Sci, 2015. 68: p. 1-66.
9. Zhou, Q., et al., Piezoelectric films for high frequency ultrasonic transducers in biomedical applications. Prog Mater Sci, 2011. 56(2): p. 139-174.
10. Wang, X., et al., Direct-current nanogenerator driven by ultrasonic waves. Science, 2007. 316(5821): p. 102-5.
11. Tadigadapa, S. and K. Mateti, Piezoelectric MEMS sensors: state-of-the-art and perspectives. Measurement Science and Technology, 2009. 20(9).
12. Bauer, S. and F. Bauer, Piezoelectric Polymers and Their Applications. Piezoelectricity: Evolution and Future of a Technology, 2008. 114: p. 157-177.
13. Rao, Y., et al., Novel polymer-ceramic nanocomposite based on high dielectric constant epoxy formula for embedded capacitor application. Journal of Applied Polymer Science, 2002. 83(5): p. 1084-1090.
14. Sebastian, M.T. and H. Jantunen, Polymer-Ceramic Composites of 0-3 Connectivity for Circuits in Electronics: A Review. International Journal of Applied Ceramic Technology, 2010. 7(4): p. 415-434.
15. Venkatragavaraj, E., et al., Piezoelectric properties of ferroelectric PZT-polymer composites. Journal of Physics D-Applied Physics, 2001. 34(4): p. 487-492.
16. Dang, Z.M., et al., Tailored Dielectric Properties based on Microstructure Change in BaTiO3-Carbon Nanotube/Polyvinylidene Fluoride Three-Phase Nanocomposites. Journal of Physical Chemistry C, 2010. 114(31): p. 13204-13209.
17. Maiti, S., et al., Low percolation threshold in melt-blended PC/MWCNT nanocomposites in the presence of styrene acrylonitrile (SAN) copolymer: Preparation and characterizations. Synthetic Metals, 2013. 165: p. 40-50.
18. Kim, H., et al., Fabrication and characterization of 3D printed BaTiO3/PVDF nanocomposites. Journal of Composite Materials. 0(0): p. 0021998317704709.
19. Kim, K., et al., 3D optical printing of piezoelectric nanoparticle-polymer composite materials. ACS Nano, 2014. 8(10): p. 9799-806.
20. Waller, D. and A. Safari, Corona Poling of Pzt Ceramics and Flexible Piezoelectric Composites. Ferroelectrics, 1988. 87: p. 189-195.
21. Haertling, G.H., Ferroelectric ceramics: History and technology. Journal of the American Ceramic Society, 1999. 82(4): p. 797-818.
22. Dietze, M. and M. Es-Souni, Structural and functional properties of screen-printed PZT-PVDF-TrFE composites. Sensors and Actuators a-Physical, 2008. 143(2): p. 329-334.
23. McKenna, E.M., et al., Comparison of r(33) values for AJ404 films prepared with parallel plate and corona poling. Journal of the Optical Society of America B-Optical Physics, 2007. 24(11): p. 2888-2892.
24. Huang, S., et al., Efficient poling of electro-optic polymers in thin films and silicon slot waveguides by detachable pyroelectric crystals. Adv Mater, 2012. 24(10): p. OP42-7.
25. Lee, C. and J.A. Tarbutton, Electric Poling-Assisted Additive Manufacturing Process for Lead-Free Piezoelectric Device Fabrication. 43rd North American Manufacturing Research Conference, Namrc 43, 2015. 1: p. 320-326.
26. 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).
27. Yen, H.J., C.J. Chen, and G.S. Liou, Flexible Multi-Colored Electrochromic and Volatile Polymer Memory Devices Derived from Starburst Triarylamine-Based Electroactive Polyimide. Advanced Functional Materials, 2013. 23(42): p. 5307-5316.
28. Lim, J.W., et al., Mechanical integrity of flexible Ag nanowire network electrodes coated on colorless PI substrates for flexible organic solar cells. Solar Energy Materials and Solar Cells, 2012. 105: p. 69-76.

29. Zhang, K., et al., Novel aromatic polyimides with pendant triphenylamine units: Synthesis, photophysical, electrochemical properties. Journal of Electroanalytical Chemistry, 2012. 682: p. 101-109.

30. Grucela-Zajac, M., et al., Photophysical, electrochemical and thermal properties of new (co)polyimides incorporating oxadiazole moieties. Synthetic Metals, 2014. 188: p. 161-174.

31. Yen, H.J., et al., High-Efficiency Photoluminescence Wholly Aromatic Triarylamine-based Polyimide Nanofiber with Aggregation-Induced Emission Enhancement. Advanced Optical Materials, 2013. 1(9): p. 668-676.

32. Wang, J.H., et al., In Situ Preparation of Polyimide/Amino-Functionalized Carbon Nanotube Composites and Their Properties. Polymer Composites, 2014. 35(10): p. 1952-1959.

33. Tabatabaei-Yazdi, Z. and S. Mehdipour-Ataei, Poly(ether-imide) and related sepiolite nanocomposites: investigation of physical, thermal, and mechanical properties. Polymers for Advanced Technologies, 2015. 26(4): p. 308-314.

34. Bodkhe, S., et al., One-Step Solvent Evaporation-Assisted 3D Printing of Piezoelectric PVDF Nanocomposite Structures. Acs Applied Materials & Interfaces, 2017. 9(24): p. 20833-20842.

35. Guo, S.Z., et al., Solvent-cast three-dimensional printing of multifunctional microsystems. Small, 2013. 9(24): p. 4118-22.

36. Chen, Z., et al., 3D printing of piezoelectric element for energy focusing and ultrasonic sensing. Nano Energy, 2016. 27: p. 78-86.

37. Fuh, Y.K., B.S. Wang, and C.Y. Tsai, Self-Powered Pressure Sensor with fully encapsulated 3D printed wavy substrate and highly-aligned piezoelectric fibers array. Sci Rep, 2017. 7(1): p. 6759.
49. S. Bauer, 2006, Piezoelectric polymers, *Materials Research Society Symposium Proceedings*, Vol. 889, Materials Research Society.

50. "Transducer and method of making the same," ed: Google Patents, 1949.

51. Kim H., Torres F., Wu Y., Villagran D., Lin Y., and Tseng T.-L.B.: Integrated 3D printing and corona poling process of PVDF piezoelectric films for pressure sensor application. *Smart Mater. Struct.*, 26, 085027 (2017).

52. K.C. Aw, R. Finch, M. Evans, T. Giffney, US non-provisional patent, Apparatus and Methods for Printing Three Dimensional Objects, Application # 15/006,371, filed on 26th January 2016.

53. Incropera FP, De Witt DP, Fundamentals of heat and mass transfer. 1985.

54. Van Lith R, Baker E, Ware H, Yang J, Farsheed AC, Sun C, and Ameer G, 3D-Printing Strong High-Resolution Antioxidant Biodegradable Bioresorbable Vascular Stents. Advanced Materials Technologies, 2016;1:1600138.

55. Vaezi M, et al. Multiple material additive manufacturing– Part 1: a review: this review paper covers a decade of research on multiple material additive manufacturing technologies which can produce complex geometry parts with different materials. Virtual PhysPrototyp 2013; 8:19–50.

56. Lee, J. et al. Fabrication of patterned nanofibrous mats using direct-write electrospinning. *Langmuir*. 28(18), 7267–7275 (2012).

57. T. Furukawa, K. Fujino, and E. Fukada, "Electromechanical properties in the composites of epoxy resin and PZT ceramics," *Japanese Journal of Applied Physics*, vol. 15, p. 2119, 1976.