Poly(vinylidene fluoride)/Zinc Oxide Smart Composite Material

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ABSTRACT

This work aimed at fabrication and electromechanical characterization of a smart material system composed of electroactive polymer and ceramic materials. The idea of composite material system is on account of complementary characteristics of the polymer and ceramic for flexibility and piezoelectric activity. Our preliminary work included Polyvinylidene Fluoride (PVDF) as the flexible piezoelectric polymer, and Zinc Oxide (ZnO) as the piezoelectric ceramic brittle, but capable to respond strains without poling. Two alternative processes were investigated. The first process makes use of ZnO fibrous formation achieved by sintering PVA/zinc acetate precursor fibers via electrospinning. Highly brittle fibrous ZnO mat was dipped into a PVDF polymer solution and then pressed to form pellets. The second process employed commercial ZnO nanopowder material. The powder was mixed into a PVDF/acetone polymer solution, and the resultant paste was pressed to form pellets. The free standing composite pellets with electrodes on the top and bottom surfaces were then subjected to sinusoidal electric excitation and response was recorded using a fotonic sensor. An earlier work on electrospun PVDF fiber mats was also summarized here and the electromechanical characterization is reported.

Keywords: Piezoelectric composite, PVDF, ZnO, Electrospinning

1. INTRODUCTION

Our motivation is Micro Air Vehicles that will have morphing wing via electroactive smart materials. Micro Air Vehicles (MAVs) may be characterized as flying systems with characteristic length (i.e. wing span) and weight not more than 15cm and 100gr, respectively[1]. They are improving and successfully made smaller as a result of multidisciplinary efforts: advances in materials, fabrication, electronics, propulsion, actuators, sensors, and control[2]. An improved MAV is expected to have high maneuverability and aerodynamic performance for which morphing the wings is being given attention in recent studies[2, 3, 4]. Strain-actuated adaptive wings that is morphing the wing into different shapes by electro-mechanical smart materials is an option. Smart materials of high specific strength would also make possible the higher flight durations with lower power consumption. With these expectations piezoelectric polymer/ceramic composites become a topic of interest in MAV wing applications both for actuation and sensing. In an earlier attempt, Pawlowski et al.[4] studied on two materials systems and electrospun polymer fibers to obtain electroactive wing skin. They reported the fiber-coated wing frames exhibited a perceptible vibration upon excitation with a 2 kV (peak-to-peak) sine wave at 6.7 Hz.

There are number of materials, such as the electroactive ceramics (EAC), shape memory alloys (SMA) and electroactive polymers (EAP), offering "active" response: they experience a significant change in their spatial dimensions due to the applied electrical stimuli or vice versa. This study was focused on one EAC, zinc oxide, and one EAP poly(vinylidene fluoride), materials systems, and their composite.

Piezoelectric ceramic materials have been under investigation for their active responses and their effective use in sensor and actuator applications. Piezoceramics most often have lead zirconate titanates (PZT), barium titanates (BT), strontium titanates (ST), and quartz based structures, which possess high strain response. Yet there has been interest to employ alternative materials with original structures; hence piezoelectric ZnO formation has also attracted attention. It is not only an optically appealing material, but also shows striking electronic properties. Different processing techniques and conditions of ZnO can be introduced. Electrospinning, for instance, is used to produce ceramic nano-scale fiber mats[5-7, 8]. These fiber mats have the potential in the use of electroactive systems. The piezoelectric ceramic material, ZnO, is extensively used due to its unique combination of electrical, optical, and piezoelectric properties. These applications include the following: liquid crystal displays and window coatings[9], gas sensors covering various materials[10-13], optoelectronic devices[14], solar cells[15], surface acoustic wave devices (SAW)[16], and ultrasonic transducers[17].

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Piezoelectric polymer PVDF, on the other hand, become appealing to numerous industries for their inexpensive, lightweight, biologically compatible and mechanically stable structures. It can undertake large amount of deformation while maintaining ample forces. It has expeditious response time, very low density, and eminent pliability when compared to electroactive ceramics and shape memory alloys. The piezoelectric PVDF and its copolymers are widely applied materials in both actuation and sensing mechanisms. They can be utilized as fibers and films mostly in linear movement requirements in various engineering applications such as active micro air vehicle wings[4], piezolaminated columns[18], and shape correction films in space applications[19]. Other applications may include: Proton exchange membranes[20], filtration membranes[21], structural health monitoring[22], endoscopic tactile sensors[23], and macrofluidic control[24], Kwon and Dzenis, for instance, embedded PVDF films of tens of microns thick into the graphite/epoxy (CFRP) composite laminates to monitor the tensile failure of unidirectional CFRP laminates[25].

Despite advantageous mechanical properties such as flexibility and reasonable strength, the electroactive response of piezoelectric PVDF is relatively low. The actuators made by PVDF also require high voltage power source that may be a limiting factor for several applications such as smart MAV wing. On the other hand, electroactive ceramics (EACs) are not easily malleable. Although there are studies on enhancing the mechanical properties of ceramic materials[26], they are generally fragile under plying. Hence, composition polymer matrix and ceramic fiber is likely to alleviate assets regarding both mechanical and piezoelectric responses. Stroyan 2004 processed and characterized PVDF/PZT composite films and demonstrated 7.5 times increase in the peak polarization compared to plain PVDF[27]. Su et al. developed PVP/ZnO composite fibers, but did not investigate the fibers for piezoelectricity[28]. Kowbel et al. developed and characterized integrated actuator/sensor thin polymer based composites. Their investigation covered several piezo-composites. Low-porosity PZT infiltrated with Ceraset polymer composites yielded enhancement in sensor while diminishing the actuator properties[31]. Flexible piezo-composites about 0.5 mm thick by powder mixing (PZT/VDF) and subsequent pressing were easily manufactured and resulted in significantly enhanced sensor properties. Films offered improved actuation capability compared to plain PVDF, and improved sensor capability compared to PZT.

The objective of this study is to investigate electromechanical response of electrospun PVDF fibers, and develop electroactive or smart composite material using PVDF and ZnO as its ingredients. The fabrication of composites is in the preliminary phase where the feasibility of the approach is evaluated by the electromechanical characterization on the composite pellets. The electroactive ceramic material of this work, ZnO is used in two forms: ZnO fiber mats obtained via in-house electrospinning based process and commercial ZnO nanopowder. The polymer matrix material PVDF is used in polymer solution form and as electrospun fiber mats. Electrospinning based polymer and ceramic fibrous mats are produced following the processes optimized in our previous work[8]. The resulting composite structure is expected to be as ZnO fibrous mats or particles embedded in a PVDF matrix. Electromechanical characterization of PVDF fiber mats and PVDF/ZnO composite pellets are performed. Pellets are expected to impart piezoelectric activity even prior to poling, due to existence of ZnO fiber mats.

2. MATERIALS PROCESSING

This section presents the attempts to obtain PVDF/ZnO electroactive composite material system. Processes involve either in house manufactured ZnO fibrous mats via electrospinning or commercially available ZnO nanopowder. In our earlier work, we investigated whether the electrospinning process has a promise to improve the electromechanical performance of PVDF[8]. The same work also reported ZnO fibrous formation by electrospinning based process. The major findings about the processes for fibrous mats are first summarized also here for convenience.

Electrospinning (also called electrostatic fiber spinning) is a process to produce continuous nanometer or micrometer size fibers from both synthetic and natural polymers. Electric forces are used to form fibers from material solutions or melts in the electrospinning process. Studies on electrically driven liquid jets were initially started in 19th century, and electrospinning of polymer fibers was first patented by Formhals[32] in 1934. The main principle in electrospinning as defined by Doshi and Reneker is to generate a charged jet of polymeric solution by applying an electric field[33]. As the jet travels in the air, the solvent evaporates and a charged fiber is left behind which can be collected on a grounded plate (collector). Through this process, mostly mats of randomly oriented fibers with large surface to volume ratio as well as various fiber morphologies and geometries are fabricated from several polymer solutions, as noted in Deitzel et al.[34].

In a homemade electrospinning set-up, as depicted in Figure 1, a polymer solution is placed into a syringe that has a millimeter size nozzle, which is subjected to a potential difference of several kilovolts between 5 to 15kV. The syringe is placed in a syringe pump (New Era NE-1000 Syringe Pump) by which the rate of the polymer flow is continuously controlled without disturbing the set-up, via an RS-232 unit attached to both the set-up and a computer. Under the applied electric field, the polymer solution is ejected from the nozzle to the collector due to high electrical force apparent on the polymer droplet at the tip of the nozzle. As the polymer jet travels in the air, the fiber diameter reduces significantly due to loss of the solvent in the air. The randomly oriented ultra-fine fibers collected on the screen produce an unexpectedly high surface area to volume ratio and are of interest for many application ranging from textile to composite reinforcement, sensors, actuators, biomaterials, filter and membrane technology[36].

2.1 Electrospinning of PVDF Fiber Mats

The electrospun PVDF fibers are still of interest in the course of this work, because it is easier and quicker to fabricate electroactive PVDF films via electrospinning, and direct or in-situ coating of the MAV wing may be possible unlike in the case of cast polymeric or composite films. Process optimization of electrospinning of PVDF was carried out targeting for uniform fiber mat fabrication. Solution properties were initially adjusted by varying the solvent type, DMF and Acetone, and their mixing ratios. It was found that the solution concentration of 20% with 50% Acetone/DMF ratio produces fiber with uniform diameter and morphology resulting planar and uniform mats. Figure 2 summarizes how the applied voltage and the collector distance played role on the morphology of the fiber mats.

2.2 Electrospinning of ZnO Fiber Mats

Zinc oxide fibrous formation by electrospinning based process is to be used in the composite material. Aqueous solutions of Poly(vinyl alcohol) (PVA) (12% w/w) and zinc acetate (35%) were prepared. When both of the solutions are totally dissolved in water, they are heated up to 80^0C and mixed for 5 hours to prepare a precursor solution. The solution was then electrospun to produce mats of precursor fibers. In order to produce zinc oxide fibers the precursor mat was exposed to a heating regime according to the TGA result given in Figure 3. TGA result suggested that any temperature above 425^0C is available for the calcination process since the organic content in the precursor fibers were lost after this temperature. The optimum fiber morphology was obtained by calcining the mats under 500^0C for 4 hours with a heating rate of 0.5^0C from room temperature.

Process of ZnO nano-fiber production was also optimized by varying the precursor ingredients and thermal treatment on the mats. It was found that a lower heating rate and hanging the sample during the thermal process prevents the fibers to break. Moreover, precursor solution concentration significantly affects the final zinc content and zinc oxide fiber morphology. Figure 4 shows SEM images of the precursor fibers and the ZnO fibrous formation after the precursor fibers were calcined. Closer look into the images revealed that Nano-scale zinc oxide fibers-like formations are composed of smaller zinc oxide particles merged into continuous array. It was concluded that the boundaries created between the ZnO particles make the fibrous formation fragile and difficult to handle. These boundaries act as crack initiators and eminently diminish the mechanical strength. It should be also noted that planar area of resultant ZnO fibrous mat is about 1/10 of the precursor fiber mat planar area.

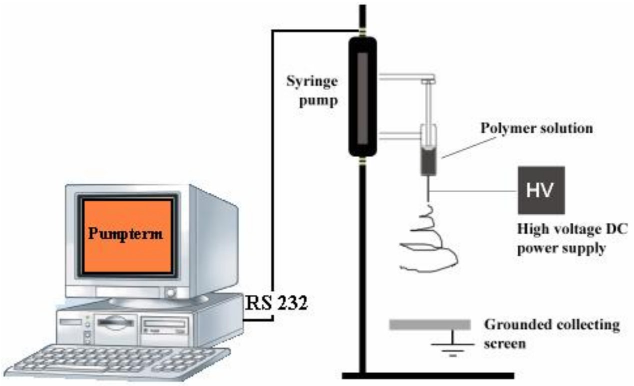

Figure 1 Schematic representation of the computer controlled electrospinning setup. Up to 100 syringe pumps can be independently controlled via one unit.

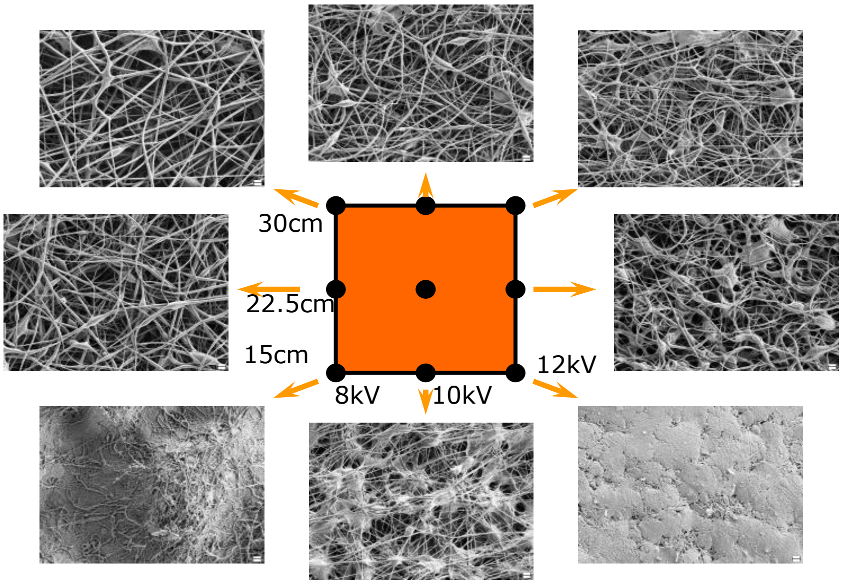

Figure 2 A detailed road-map of micrometer fiber fabrication scheme for 50% Acetone/DMF ratio mixture, PVDF solution[8]

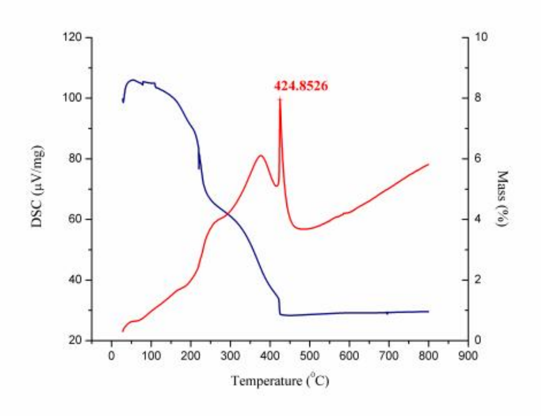

Figure 3 TGA results show that the inorganic part is attained after 425^{0}C [8]

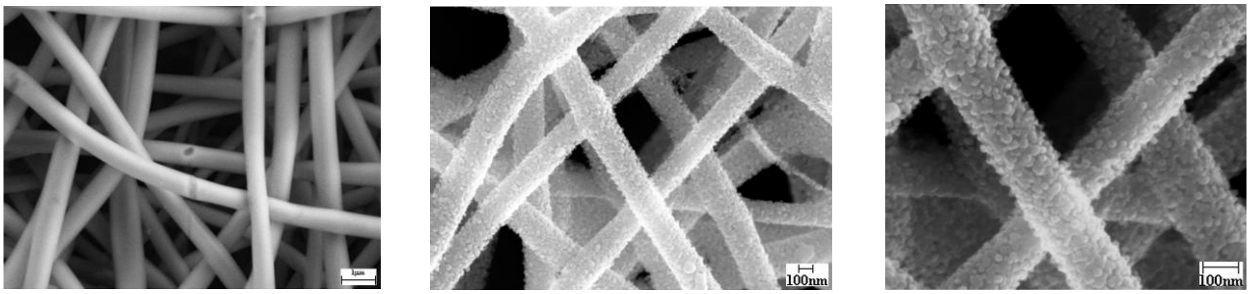

Figure 4 ZnO fibrous formation via electrospinning based process, a) Precursor fiber mat, b) ZnO fibrous formation after calcinations c) ZnO sample imaged by 200K magnified. Grains with an average diameter of 20nm can be easily seen on the fiber structure.[8]

2.3 PVDF/ZnO Composite Materials

Two different processing techniques are established in order to compare both the processibility and the composite's electroactivity. The main difference of the processes is the different ZnO forms to be included in the composite system:

one approach uses fibrous, but highly fragile mats, and the other employs commercially available ZnO loose nanopowders.

Electrospun fibrous mat of ZnO described in the previous section is dipped into a PVDF/acetone solution in order to make PVDF coating of the fragile ZnO fibrous formations. The dipping operation is done by KSV Sigma 70 Surface Tensiometer. PVDF coated ZnO fibrous mat is then pressed into a pellet. Another pellet is also pressed by laminating electrospun PVDF fiber mats and the dipped ZnO fibrous mat in order to increase the polymer content.

In the second process, ZnO (Inframat Advanced Materials, average particle size: ~30nm) and PVDF (Alfa Aesar, m.p. 155 -160°C) are utilized as powders. Through this method, nanocomposite of %65 volumetric ZnO loading are produced. Ceramic/polymer composites are prepared by first dissolving PVDF in hot acetone, placing ceramic nanopowder into this solution and mixing it for 5 minutes via a POLYTRON PT600 type benchtop homogenizer. After nitrogen gas is introduced to remove acetone until a gel-like soft paste is obtained, this paste is pressed into wet pellets using a Specac pellet press at a pressure of about 2000 psi. After drying in a vacuum oven at 100°C for an hour, the pellets are hot-pressed at 200°C for 15 minutes at about 15000 psi.[37]

3. CHARACTERISATION

The electroactive materials processed in this study were characterized by SEM images, XRD and direct displacement measurements while the specimens are driven by sinusoidal voltage. The direct electroactivity measurements were performed using the set-up composed of TREK 610E high voltage supply/amplifier, an oscilloscope, a function generator and MTI-2100 high resolution fotonic sensor with a sensitivity of 0.00042μm/mV. The set-up is shown in Figure 5.

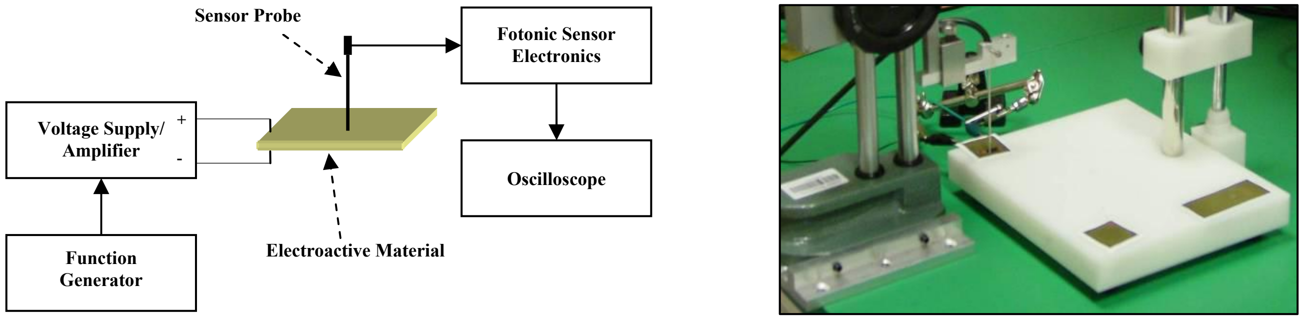

Figure 5 a) Electroactive response measurement set-up, b) closer view of fotonic displacement sensor probe and PVDF electrospun specimen.

3.1 Electrospun of PVDF Fiber Mats

Poly(vinyldene fluoride) fibers were previously electrospun to be utilized as a micro air vehicle wing material[4]. Several other studies were recently published on electrospinning PVDF fibers, Harisson et al.[37, 38], Zhao et al.[39], Nasir et al.[40], Re and Dzenis[41], Yee et al.[42], Choi et al.[43]. In all these works along with our earlier work[8] morphology and crystalline structure of the electrospun non-woven fibrous mats were characterized mainly by SEM imaging and XRD, respectively. DSC was also used as a tool for evaluating the correlations between the thermal characteristics (melting temperature and heat of fusion) and the electrospinning imposed crystalline structure. Most of these studies aimed at the piezoelectric characteristics of the PVDF fine fibers. It is known that PVDF offers piezoelectric response when its crystalline structure is β-phase dominant[44]. Gregorio[44] reported number of studies published on obtaining and characterization of the different PVDF phases, showing conflicting results, and investigated the effect of processing conditions in PVDF film formation.

XRD results demonstrated that electrospinning provides in-situ β-phase formation unlike in the case of PVDF cast films, which typically require post-processing such as mechanical stretching. X-Ray Diffraction data given in Figure 6 exhibits that the characteristic α-phase peaks obtained from the electrospun samples are dominant over the β-phase ones. However, for large collector distance values (Figure 2), it was observed that as the applied voltage increases, the β-phase formation in the electrospun fibers increases. This reveals that an increase in the electric force applied on the polymer solution, elongates the polymer chains from the tip of the needle until the polymer touches the collector screen. As the figure suggests, when the voltage is increased from 8 kV to 12kV, the β-phase peak tends to increase while the α-phase peaks diminish.

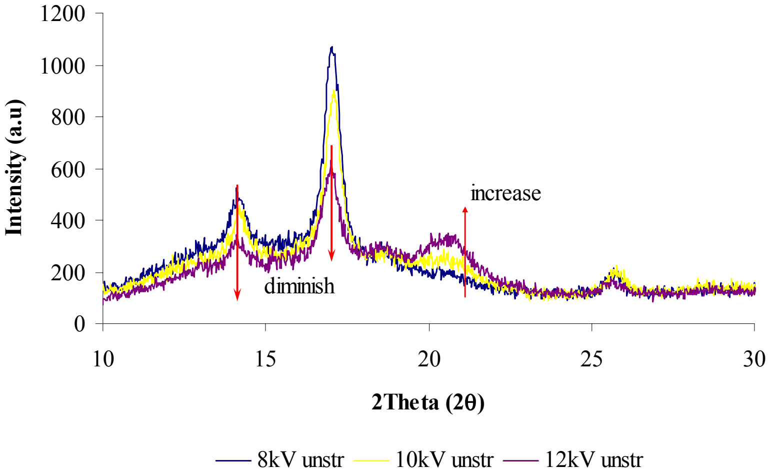

Figure 6 Effect of electrical force applied on the electrosun fiber crystal structure.[8]

In this work we extended our efforts by electroactive response measurements on the electrospun PVDF fibrous mats. The set-up in Figure 5 was used. Readings from fotonic sensor indicated the electrospun PVDF fiber mat responded to applied electric field (Figure 7a). The nature of the response, however, appeared to be electrostrictive rather than piezoelectric. This was evident when the polarity of the excitation was switched to opposite polarity, the response remained the same. In addition, the peak of the response was observed to have a quadratic relation with the excitation peak voltage as shown in Figure 7b. As to the measurements, this outcome downplays the piezoelectric ability on as-received electrospun PVDF fiber mats without mechanical stretching and poling.

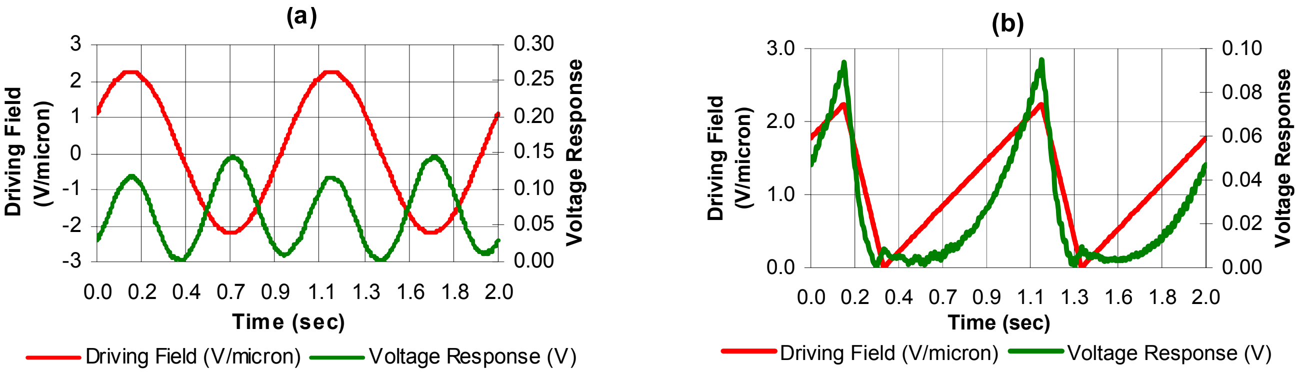

Figure 7 Electromechanical response of as-received electrospun PVDF fibers, a) sinusoidal excitation at 2000 V and 1 Hz. b) effect of peak voltage on the output response

3.2 ZnO Fibrous Mats

Resultant ZnO fibers were characterized by SEM and XRD to figure out their crystal structure of interest. It was found that the produced fibrous formations were mostly precipitate-free, and uniform in diameter. The XRD measurements in Figure 13 confirmed exactly the desired crystallinity, which is the wurtzite structure offering the piezoelectric ability as it is. It is significant to observe this crystal structure since the electroactive characteristics of ZnO comes from these specific crystal properties.

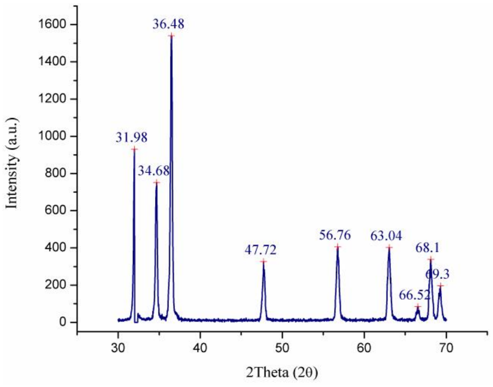

Figure 8 XRD data obtained from ZnO samples. The peaks are similar to the characteristic peaks of the wurtzite structure.[8]

3.3 PVDF/ZnO Composite

XRD measurements also confirmed that ZnO powder has the desired crystallinity, the wurtzite structure as in the case of fibrous mat. This suggested the ZnO ingredient in the composite material systems without poling should impart piezoelectricity. Electromechanical ability was measured on the pellets formed by the two proposed composite making process. Similar to PVDF fiber mats, sinusoidal response reading from both powder based and fibrous based pellets were taken. The nature of the response is concluded to be piezoelectric as the polarity of the excitation changes, response peak also switches sign.

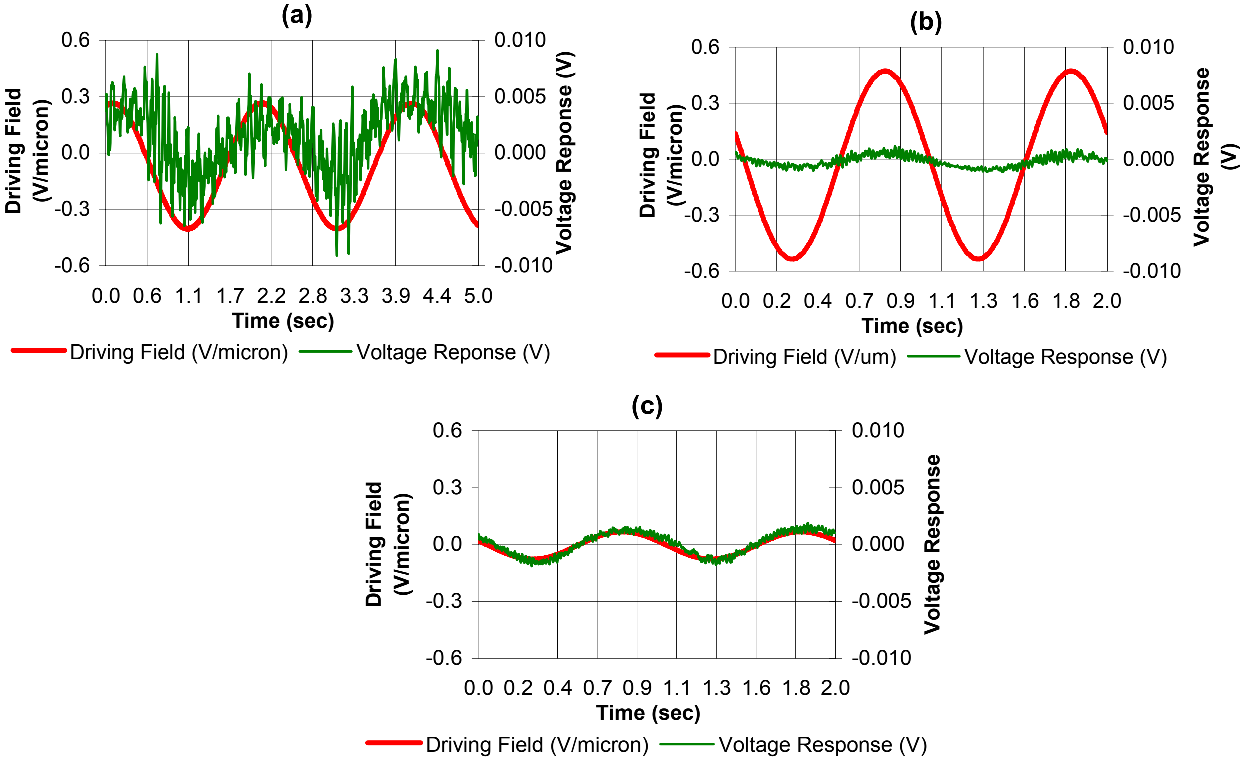

Figure 9 Electromechanical response of PVDF/ZnO composite pellets: a) PVDF coated ZnO fibrous mat excited with 10V, 0.5Hz, b) PVDF coated ZnO fibrous mat laminated with PVDF excited with 50V, 1Hz, and c) PVDF and ZnO nanopowder-based composite excited with 50V, 1Hz sinusoidal.

4. DISCUSSION

Process flow for PVDF/ZnO electroactive composite material was proposed and realized. The electroactivity of the composite material along with electrospun PVDF fiber mats were investigated and reported. The major findings are summarized below:

- Electrospinning promotes β-Phase formation in PVDF fiber crystal structure. The results suggest there is in-situ polymer chain elongation and alignment that makes electrospinning favorable in piezo-film/mat production. Electromechanical response, however, recorded prior to poling was found to be electrostrictive rather than piezoelectric. On the other hand, evidence of piezoelectricity is on research.
- Brittleness of ZnO ceramic fibrous formation was handled by dipping the ZnO mat into PVDF solution. Highly loaded ZnO nanopowder PVDF matrix composite was also manufactured. Relatively flexible composite pellets were obtained.
- The electroactive response of the composite material is observed without poling, but may not be sufficient for actuation in MAV application. The sensing ability will next to be investigated.
- Investigation for the effect of poling and ZnO fraction on the electroactive response of the composite material is underway.

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