

**Characterization of Nanoporous Polyvinylidene Fluoride (PVDF)  
Sensors under Tensile Loading**

A DISSERTATION

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Zhaolin Gao

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**Dr. Ping Zhao**

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## **DEDICATION**

This dissertation is dedicated to my mother.

For your everlasting love

## ABSTRACT

Piezoelectric materials are one of the currently smart materials. They have achieved great success in biologic medical and electrical applications, as fluorocarbon coatings and other areas. They have shown thriving prospects in the ongoing research and commercialization process. To improve the material's piezoelectricity, a Polyvinylidene Fluoride (PVDF) sensor with integrating nanoporous structures was developed and fabricated. Several sets of samples with different porosities from 0% to 42.0% were made. The porosity effect on the sensor samples was studied under tensile loading, and the piezoelectric coefficient  $d_{31}$  was characterized. The results showed that the  $d_{31}$  value increased from ~15.8 pC/N to ~51.3 pC/N as the porosity increased from 0% to 23.7%. With a further increase in porosity, the  $d_{31}$  value had a considerable declining trend. It is clear that the sensor exhibited the highest piezoelectric effect when the porosity was 23.7%. The study suggests that nanoporous-structured PVDF sensor has good characteristics to generate electric voltage, and the sensor with 23.7% porosity shows the best performance for sensing purposes. Meanwhile, to investigate the sensing effect of the PVDF sensor, a set of cyclic loading was applied to the sensors, and the results indicated that the sensors can properly detect dynamic loads ranging from 0 to 10 N. The output signals from the sensors and results in the relationship between their porosity and the characteristic of the membrane preparation conditions can offer interesting perspectives for the advancement of sensor design.

Keywords: PVDF, Nanoporous structure, Piezoelectric polymers, Porosity effect

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# CHAPTER I INTRODUCTION

## 1.1 Background

Polyvinylidene fluoride (PVDF) is an emerging piezoelectric material that uses the piezoelectric effect to measure changes in pressure, acceleration, temperature, strain, or force by converting them to an electrical charge. Many technologies and fields widely use PVDF thin films, such as ultrasonic air transducers, actuators, sensors and energy harvesting because of their two main characteristics, which are polymorphism and piezoelectric properties<sup>[1]</sup>. The PVDF's piezoelectric coefficient, which is an important constant in the piezoelectric materials, quantifies the volume change when a piezoelectric material is subjected to an electric field<sup>[2]</sup>. These two properties depend on its crystalline structures,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  phases<sup>[3]</sup>. In the field of PVDF,  $\beta$ -Phase is the most broadly studied piezoelectric polymer material. This is mainly due to the  $\beta$ -fraction has high piezoelectric coefficient, excellent stability, and desirable flexibility. Nanostructured PVDF polymers have been used in a variety of nanogenerator designs for mechanical energy harvesting. All these merits make the PVDF material useful for tactile sensor arrays, strain gauges, and transducers<sup>[4][5]</sup>. Therefore, increasing the proportion of the  $\beta$ -phase of PVDFs has great scope for research<sup>[6]</sup>.

Mechanical stretching and electrical poling are efficient approaches to increase the amount of  $\beta$ -phase in PVDF films<sup>[7][8][9][10]</sup>. The efficiency of the  $\beta$ -phase transformation can be affected by many factors such as stretching ratio, temperature,

poling duration, poling voltage, etc., which need to be precisely controlled. Here, a couple of ideas have been proposed and solved in different area of researches. Sun et al.<sup>[7]</sup> suggested that mechanical stretching of films is an efficient approach to increasing  $\beta$ -phases. The polymer chains are straightened which the random dipoles to orient themselves in the stretching direction. The orientation of the dipoles in the films causes depends on the strain rate, stretching ratio, and temperature of the films<sup>[11]</sup>. The efficiency of the phase transformation decreases at higher stretching temperatures due to the mobility of macromolecular chains. Sajkiewicz et al.<sup>[9]</sup> investigated  $\alpha$  phase to  $\beta$ -phase transformation during stretching of PVDF films at temperatures of 50–145°C. Mohammadi et al.<sup>[10]</sup> observed that the transformation of polymer crystals increased with increases in stretching ratio and stretching rate. Ueberschlag<sup>[7]</sup> presented piezoelectric characteristics of PVDF films, measurement of piezoelectric and pyroelectric coefficients, and sensing mechanisms of the films for different applications. Therefore, the process of conducting the mechanical stretching or electrical poling can be difficult or time consuming.

An alternative way that has drawn attention is to combine different materials with PVDF during the synthesis process to improve the  $\beta$ -phase transformation owing to the modification of the structures of PVDF films. Introducing porous structures into PVDF films by adding other materials is one of the effective methods that can enhance the formation of  $\beta$ -phase<sup>[12]</sup>. The triboelectric energy generators prepared using the combination of self-polarized, high  $\beta$ -phase nanocomposite films of Gd<sub>5</sub>Si<sub>4</sub>-PVDF and polyamide-6 (PA-6) films have generated significantly higher voltage<sup>[13]</sup>. This new material displayed a ferromagnetic behavior as compared to diamagnetic nature of

pristine PVDF. The presence of magnetic nanoparticles in the polymeric matrix allows for some control over the microstructural properties during the preparation process. The results open new routes for multiferroic composite films to be suitable for multifunctional magnetic and triboelectric energy harvesting applications<sup>[13]</sup>. However, the process involved the fabrication of nanowires and their integration with PVDF films, which is not economic for making large-size films.

To address the problem, a nanoporous PVDF thin film was developed using a simpler template-assisted method for energy harvesting in self-powered small electronic devices in the previous work<sup>[14]</sup>. Instead of synthesis nanowires, commercialized Zinc Oxide (ZnO) nanoparticles were incorporated into a PVDF solution to serve as a template and followed by removing ZnO in an etching solution. These new structures that PVDF films with pores dramatically enhanced the piezoelectric effect since it yielded considerably large deformations under a small force, and thus produced much higher output signals. Mao et al.<sup>[14]</sup> fabricated PVDF thin films with pores using a simple casting-etching process in the wafer scale. The new PVDF nanogenerators can be directly attached to the surface of an electronic device such as a cell phone and effectively convert mechanical energy from ambient surface oscillations to electricity using the device's own weight to enhance the amplitude. Together with electrical poling, the results demonstrated that the piezoelectric effect of the nanoporous PVDF film dramatically increased and its voltage output was more than two times higher than that of the bulk PVDF film. Researchers have proved that a larger signal could be produced if the structure of the PVDF changed. This means that having pores allows the material to deform more significantly from its natural state compared to the previous material

performance as a nanogenerator<sup>[15]</sup>. In this study, a mixture of PVDF solution and ZnO nanoparticles were selected for the fabrication in order to enhance the piezoelectric performance. PVDF should possess well controlled nanomorphology, high purity of the  $\beta$ -phase, and excellent flexibility and durability. There are two merits that introducing ZnO nanoparticles to PVDF: 1) to create porosity in the PVDF film to modulate its mechanical property, and 2) to seed the formation of the piezoelectric  $\beta$ -phase. Based on their unique advantages such as low-cost, non-toxicity, good scalability, and facile removal by acidic solution, ZnO nanoparticles perform perfectly during the fabrication of porous nanomaterials compared to the other inorganic and organic materials, such as SiO<sub>2</sub> and polystyrene.

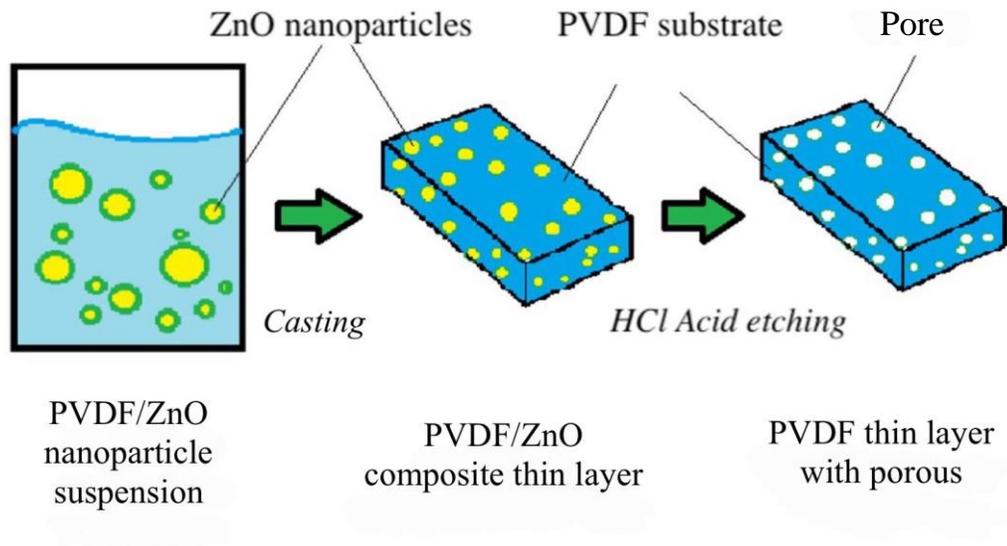
## **1.2 Objectives**

Therefore, in this study, this nanoporous PVDF film will be used to fabricate the sensors and the porosity effect on the piezoelectric properties of the sensor samples will be studied, which has not been explored previously. It is expected that the ability of the sensor will be improved dramatically thanks to the enhancement of its piezoelectric effect.. The synthesis process of PVDF films will be adopted from previous studies and tensile tests will be used to determine the piezoelectric coefficient  $d_{31}$ . Cyclical loading will be applied to investigate the sensor's performance. It is anticipated that the study will help to determine the optimal design of the sensor.

## CHAPTER II PVDF SENSOR FABRICATION AND TENSILE TESTING SETUP

### 2.1 PVDF Synthesis Method

To fabricate thin nanoporous PVDF films, PVDF powder (Sigma Aldrich, St. Louis, MO) was dissolved in 2-butanonesolvent (Sigma Aldrich, St. Louis, MO) at 75 °C, then mixed with ZnO nanoparticles of 35-45 nm (US Research Nanomaterials Inc, Houston TX.). The mass ratio between the PVDF powder and ZnO nanoparticles was adjusted to 0 weight percent (wt%) to 70wt% at 10wt% intervals to create the differences in porosity. After the mixed solution was fully dissolved and looked transparent, it was treated in an ultrasonic bath for 2 hours to create a uniformly mixed PVDF and ZnO nanoparticle suspension. The suspension was cast into films in petri dishes and dried at 75 °C. The dried films were then placed in an acid bath of 37wt% with 3 mol of hydrochloric acid solution (HCl) (Macron, Avantor, Inc, Radnor, Pennsylvania) for 3 hours to remove the ZnO nanoparticles from the film, thus creating the pores in the PVDF films. HCl solution was selected because PVDF is a hydrophobic polymer with excellent chemical stability against corrosive solvents including acids. The films were then washed in deionized (DI) water before testing. Figure 1 illustrates the synthesis process and the structure of the PVDF films.



*Figure 1. Process and structure of nanoporous PVDF thin films*

During the PVDF film synthesis, 15 ml of 2-butanone solvent with measured mass of PVDF powder and ZnO nanoparticles was used. Figure 2 illustrates the relationship between the PVDF sample with the ZnO mass ratio and the thickness measured from the sample. Each sample were measured by the micrometer from five different area equally, which indicates that under the same ZnO mass ratio, all the PVDF samples are consistent.

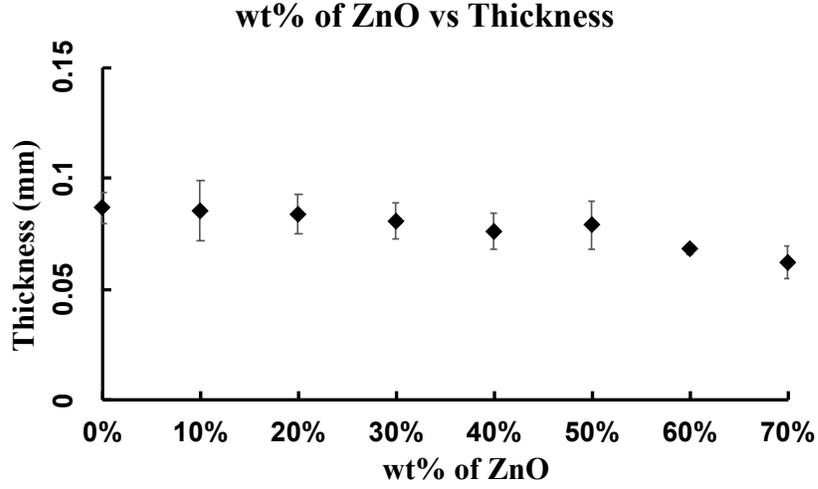


Figure 2. Relationship between the mass of ZnO ratio and the PVDF sample thickness

The mass ratio between the PVDF powder and ZnO nanoparticles was adjusted to 0 to 70wt% at 10 wt% intervals to create the porosities ranging from 0 to 42.0 vol%. Table 1 provides the used ZnO mass ratio and corresponding porosity of the PVDF films in this study. The porosity  $\phi$  of the films was determined by the ratio using Eq. (1)

$$\phi = \frac{V_P}{V_T}, \quad (1)$$

where  $V_p$  is the effective volume of pores, and  $V_T$  is the total volume of the material, including the solid and void components. The pore volume  $V_p$  in the PVDF film was introduced by ZnO nanoparticles, so it was calculated as

$$V_P = \frac{m_{ZnO}}{\rho_{ZnO}}, \quad (2)$$

where  $m_{ZnO}$  is the mass of ZnO particles and  $\rho_{ZnO}$  is the density of ZnO that is 5.606g/cm<sup>3</sup>.

The total volume of the film  $V_T$  includes both PVDF  $V_{PVDF}$  and ZnO  $V_P$  components. It was calculated as

$$V_T = V_{PVDF} + V_P = \frac{m_{PVDF}}{\rho_{PVDF}} + \frac{m_{ZnO}}{\rho_{ZnO}}, \quad (3)$$

where  $m_{PVDF}$  is the mass of PVDF and  $\rho_{ZnO}$  is the density of PVDF that is 1.74g/cm<sup>3</sup>.

*Table 1.* ZnO mass ratio and porosity of PVDF films

ZnO mass ratio	Porosity
0%	0.0%
10%	3.3%
20%	7.2%
30%	11.7%
40%	17.1%
50%	23.7%
60%	31.8%
70%	42.0%

By using PVDF film synthesis, a thin nanoporous PVDF film (7.5 cm in diameter) was synthesized, which demonstrated the capability of producing high quality piezoelectric polymer thin films in large scales. Figure 3 shows a photograph of a thin PVDF film with 10 wt% ZnO. The sample thickness and scale could easily be adjusted

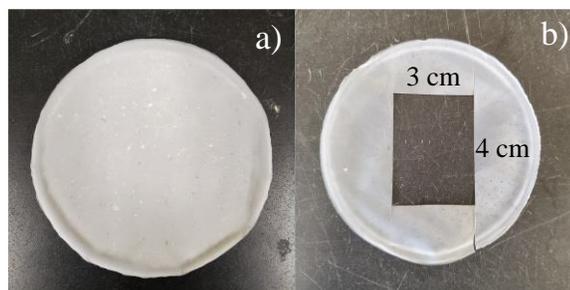
by changing the quantity of the casting mixture. The pure PVDF film sample was transparent and the sample gradually became translucent, thinner, and more fragile as the ZnO amount increased. However, the common physics characteristic would be soft and flexible, and it surely can be seamlessly attached to rough and curvy surfaces.



*Figure 3.* 10wt% of ZnO with the color of translucent

## 2.2 Nanoporous PVDF Sensor Design

To make a PVDF sensor, the synthesized thin nanoporous PVDF film (Figure 4a) was cut into 4 cm  $\times$  3 cm pieces (Figure 4b). Both sides of the thin PVDF film were taped with Copper (Cu) foils to serve as electrodes (Figure 4c); and additional Cu strips were attached to the electrodes to work as electric leads. No short circuit or noticeable voltage fluctuation was detected by a multimeter (Figure 4d).



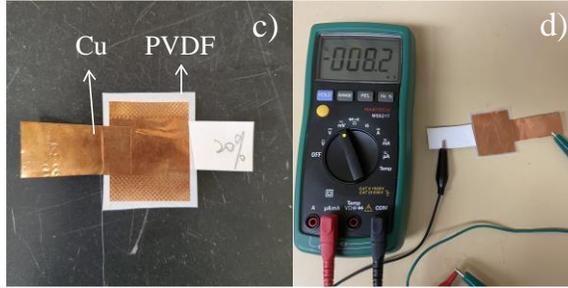


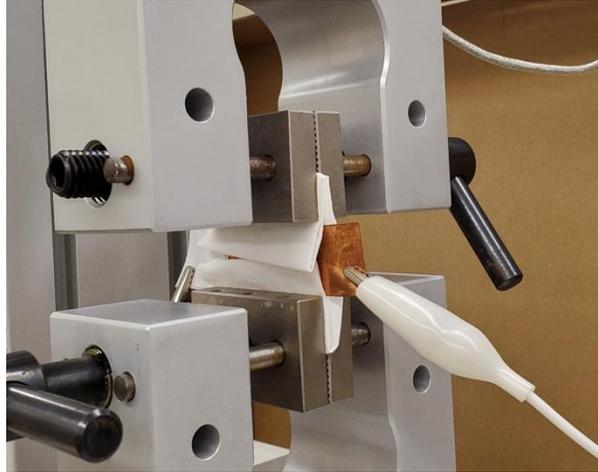
Figure 4. The procedure of a PVDF sensor fabrication

### 2.3 Tensile Tests

To maximize the piezoelectric effect of the PVDF film, electrical poling to the PVDF film has been carried out in a previous work<sup>[14]</sup>. In this research, no electrical poling was conducted as the previous work also showed that the  $\beta$ -phase of the PVDF film was able to be clearly identified in Fourier Transformation Infrared (FTIR) spectrum after the synthesis process. The  $\beta$ -phase formation was due to the interactions between the PVDF dipoles and surface charges on ZnO surfaces. This study focused on the porosity effect on the piezoelectricity of the PVDF film, therefore the sensor samples without electrical poling were used for testing.

Tensile tests were performed to determine the piezoelectric coefficient  $d_{31}$  of the PVDF sensor with different porosities. Figure 5 illustrates a piece of the PVDF sensor was placed in between two grips (Test Resources, G240G Mechanical Vice Action Grip) of a tensile tester (Test Resources, Model:SM-1000-294). A PVDF sensor (5 cm  $\times$  3 cm  $\times$  0.0101 cm) was packaged in between two Kimwipes and clamped tightly from top to bottom to isolate the sensor from the testing system. This is necessary because the

sensor of the tensile tester is located at the top of the grips, and the Kimwipes minimize the error deviation from the starting point of the signal output.



*Figure 5. PVDF sensor clamped by two grips*

A modified Sawyer-Tower circuit shown in Figure 6 was used to obtain the charge from the sensor during the test. When a tensile load was applied vertically to the clamped PVDF sensor, it was stretched and produced homogeneous electric output, which are the electric charges on both sides of the sensor's electrodes. The charges were collected in the capacitor through the wires and the corresponding data could be read on the voltmeter. Upon loading, the voltage of the capacitor and the force applied to the sensor were measured and recorded by the LabVIEW program with a frequency of 100 Hz and in 10 second intervals. The capacitance of the capacitor used in the circuit was  $\sim 100 \mu\text{F}$ , and a voltmeter ran parallel to the capacitor. Naturally a ground wire was provided for a complete circuit for the sake of protecting appliances.

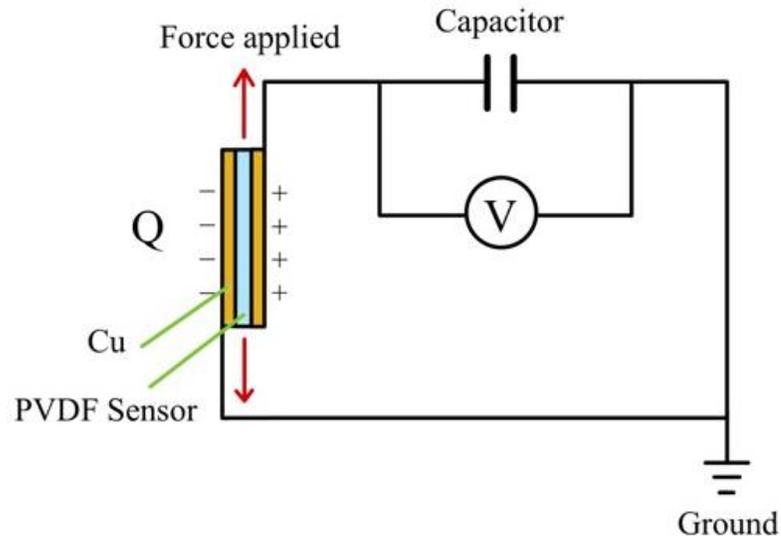


Figure 6. Modified Sawyer-Tower circuit

Another unique merit of the nanoporous PVDF sensor is its excellent flexibility. When piezoelectric materials are subjected to mechanical loading, electrical voltage can be induced because of their direct piezoelectric effect. A large voltage output indicates a stronger sensing effect. Hence, a cyclic load was applied to the sensor to investigate its sensing effect. Repeated loading tests were conducted at a speed of 5N per sec with a maximum load of 10 N. Meanwhile, the applied load and the voltage generated from the sensor were recorded using a LabVIEW program as well.

## 2.4 Piezoelectric Coefficient

Piezoelectricity is the electric charge that accumulates in certain solid materials such as crystals, certain ceramics and biological matter in response to applied mechanical stress. The piezoelectric responses of materials to electrical displacements

are critically determined by the material's output voltage  $V$  and the area of the electrode  $A$ . They play an important role in the electrical displacement  $D$  that can be written as,

$$D = Q/A = CV/A \quad (4)$$

where  $Q$  is the produced charge in the sensor,  $C$  is the capacitance of the capacitor in the circuit (Figure 6),  $V$  is the voltage output from the sensor, and  $A$  is the area of electrode that was defined by the product of length  $L$  and width  $l$  shown in Figure 7.

The piezoelectric coefficient  $d_{31}$  is the piezoelectric coefficient or piezoelectric modulus, and quantifies the volume change when a piezoelectric material is subject to an electric field, or the polarization on application of a stress. The  $d_{31}$  (C/N) was calculated based on the electrical displacement  $D$  and stress  $\sigma$  (N/m<sup>2</sup>) added on the PVDF samples with different porosities. Figure 7 illustrates multiple parameters such as forces, length and width. According to the constitutive law of a material and measurements from the sample synthesized, related equations are presented as follows:

$$d_{31} = D/\sigma \quad (5)$$

$$\sigma = F/a \quad (6)$$

where  $D$  is calculated by Equation (4), and  $\sigma$  is the applied stress on the PVDF sensor,  $F$  is the applied force from the tensile tester,  $a$  is the cross-sectional area of the PVDF sensor.

Substituting Equations (4) and (6) into Equation (5), we can get:

$$d_{31} = \frac{CV/A}{F/a} \quad (7)$$

To investigate the porosity effect, PVDF samples with different porosities were prepared from mixtures that contained with fractions of ZnO mass as described in Section 2.1. The voltage output of these thin nanoporous PVDF films with identical thicknesses (0.096mm ~ 0.058mm) was measured at a frequency of 100 Hz per 10 seconds by using an increasing force of 100N with the constant velocity of 10N/s, and their  $d_{31}$  values were recorded as a function of porosity.

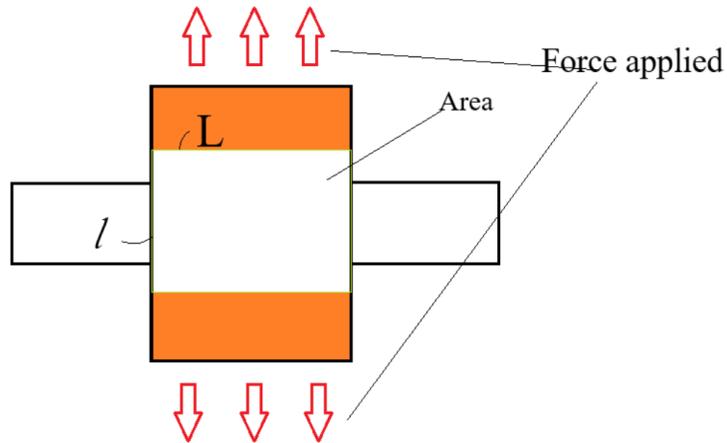


Figure 7. A Schematic diagram for the PVDF sensor

## CHAPTER III EXPERIMENTAL RESULTS AND DISCUSSIONS

### 3.1 Determination of Piezoelectric Coefficient $d_{31}$

At least five samples were tested for each sensor with the porosity ranging from 0% to 42.0%. Here a PVDF sensor sample with 11.7% porosity is used as an example showing the process to determine the piezoelectric coefficient  $d_{31}$ . The force applied to the samples was 45 N. Figure 8 illustrates the relationship between the applied stress and electric displacement of a PVDF sensor sample with 11.7% porosity, the highest peak values of the voltage output were found to be about 0.045V, the slope is the linear piezoelectric coefficient  $d_{31}$  shown in Eq. (7) and was calculated to be about 35.1pC/N. This output performance and the calculated  $d_{31}$  value were slightly higher than the recently reported values (25~32 pC/N) for other PVDF-based materials<sup>[Error! Bookmark not defined.]</sup>, such as a single PVDF poled piezoelectric film (3  $\mu\text{m}$  thick, 60 mm  $\times$  150 mm,  $d_{31} = 35.1\text{pC/N}$ ). From the results, with the load increasing gently, the output signal increased steadily as well, and there is no noticeable degradation from the signal output. This means that the PVDF sensor was suitable for working and sensing purpose during certain periods of time.

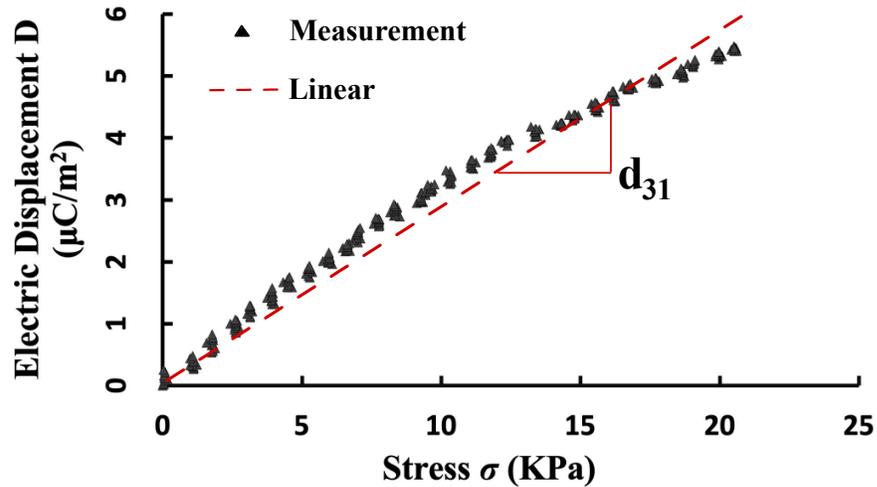


Figure 8. The relationship between the applied stress and the electric displacement of a PVDF sensor with 11.7% porosity

### 3.2 Relationship between Porosity and Piezoelectric Coefficient $d_{31}$

Figure 9 provides the piezoelectric coefficient  $d_{31}$  in related to porosity (0 – 42 %) of the PVDF sensors. It shows that as the ZnO mass fraction increased steadily from 0% to 23.7%, the  $d_{31}$  value increased from 17.4 pC/N to 51.2 pC/N, and then decreased to 33.3 pC/N as the porosity increased to 42.0%. The optimal porosity for achieving the maximum  $d_{31}$  value was then identified as 23.7%, which indicates that under 45 N static load the voltage output increases to about 0.2V.

It is also interesting to note that even though the piezoelectric coefficient dropped down significantly after 23.7% porosity, the  $d_{31}$  value still maintains at a high-level compared to the 7.2%. In fact, the  $d_{31}$  value of the 23.7% sample is double that of the 7.2% sample and triple that of the pure PVDF sensor. Compared to the  $d_{31}$  values obtained in past studies in the piezoelectric field<sup>[16][17]</sup>, this result improves and proves

the potential future application of nanoporous PVDF sensors. In an effort to understand this trend, we learned the research conducted by Mao, to have a comprehensive understanding of the porosity-related performance. The porosity output relationship was found directly related to the ZnO mass fraction (10% to 50%) of the  $\beta$ -phase PVDF. Meanwhile, the total amount of PVDF per unit volume decreased as the ZnO ratio increased. According to the information by FTIR spectra<sup>[3]</sup>, the amount of  $\alpha$ -phase in as-prepared PVDF films monotonically decreased as the ZnO ratio increased. The amount of  $\beta$ -phase increased as the ZnO mass ratio increased from 10wt% to 50wt% (3.3% to 23.7% porosity), and then decreased when the ZnO mass fraction further increased. The nanoporous PVDF film made from the mixture of 50wt% ZnO (23.7% porosity) possessed the maximum  $\beta$ -phase quantity, corresponding to the highest piezoelectric potential. Therefore, under the same quantity, the 23.7% porosity PVDF sensor has more  $\beta$ -phase, and it produced much higher electrical response.

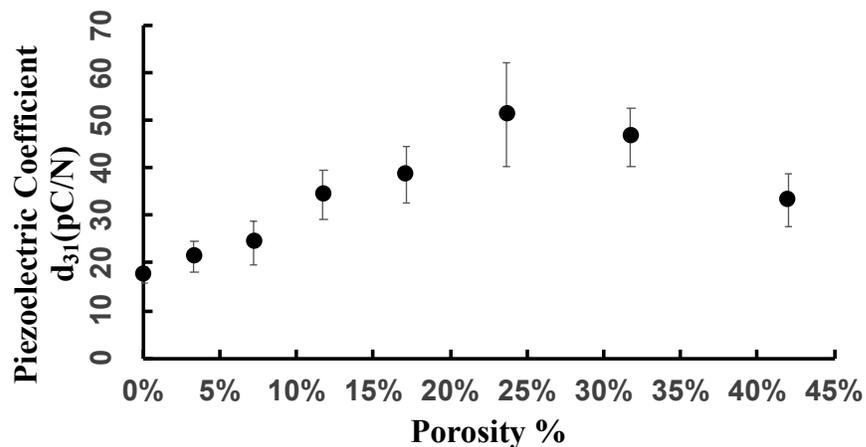


Figure 9. The piezoelectric coefficient  $d_{31}$  vs the porosity of the PVDF sensors

As discussed earlier, the presence of nanoporous structures was able to enhance the piezoelectric  $\beta$ -phase formation in the PVDF film, thus to improve its piezoelectric effect. The piezoelectric coefficient  $d_{31}$  value represents a stronger piezoelectric effect, which means that a larger electric voltage output can be generated even when the material is subjected to a lower load. This is a significant merit of a material to serve as a sensor. The results showed that the  $d_{31}$  value of the PVDF sensor was improved as the porosity increased to 23.7%, which meant that more piezoelectric  $\beta$ -phase of PVDF was induced and a stronger piezoelectric effect was produced. The maximum piezoelectric coefficient  $d_{31}$  reached 51.2 pC/N, which is significant improvement compared to the  $d_{31}$  value of most commercialized PVDF after mechanical stretching or electrical poling that is usually  $\sim$ 20-30 pC/N. However, the  $d_{31}$  value decreased as the porosity continuously increased to 42.0%. This is because the amount of PVDF was reduced such that the  $\beta$ -phase PVDF decreased as well.

### **3.3 Sensor Capability Under Dynamic Loading**

A triangular-wave tensile load with range from 0 to 10 N and frequency at 0.5 Hz was applied to the PVDF sensors with different porosities to study their sensing effect. Figures 10 and 11 show the voltage outputs from the PVDF sensors with porosity ranging from 0% to 42.0%. All samples produced a voltage (0.1V - 0.8V) that can be detected by LabVIEW even under low applied forces (under 100 N and 2 Hz). The wave of amplitude with 0% in Figure 10 represents the output of the pure PVDF sensor, the waves of amplitude of 3.3% and 7.2% have almost the same values. Then the waves

represented are the waves of amplitude at the porosity of 42.0%, 11.7% and 17.1%, respectively.

The yellow wave of amplitude shows the sensor's signal at 31.8%, and the difference between 17.1% and 31.8% is larger than the difference between 23.7% and 23.7% of porosity. The highest wave of amplitude illustrates that at 23.7%, the PVDF sensor's signal output is around 0.8V, which is the highest signal by far in the entire figure. The difference between 17.1% and 23.7% is the maximum difference between all the waves. All these signals have in common that when the increasing load was applied, the output signals increased, and when the load decreased, the output signals dropped as well. This indicates that all these values obey the same rules that with the amount of ZnO increases, corresponding output signals increase significantly, which agrees with the changes of the  $d_{31}$  value as shown in Figure 9.

Not surprisingly, the PVDF film with 23.7% porosity occupied an absolute high position in the graph, meanwhile, signal outputs from 42.0% porosity are considerably lower than the 11.7% porosity but higher than 7.2%. Figure 11 illustrates the applied triangular-wave tensile load fluctuating from 0 to 10 N. The flat amplitude at the top and bottom peaks of the load wave presented due to the facility limitation. Thus, the effect of the signal from the PVDF film has a curved line at the peak instead of a sharp angle.

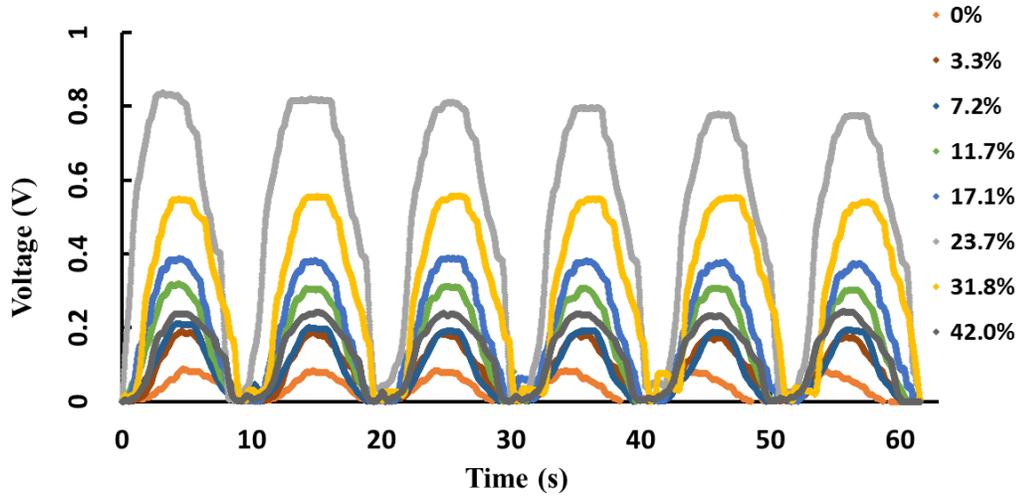


Figure 10. Induced voltage outputs of the PVDF sensors ranging from 0% to 42.0% under a triangular cyclic load (0-10 N)

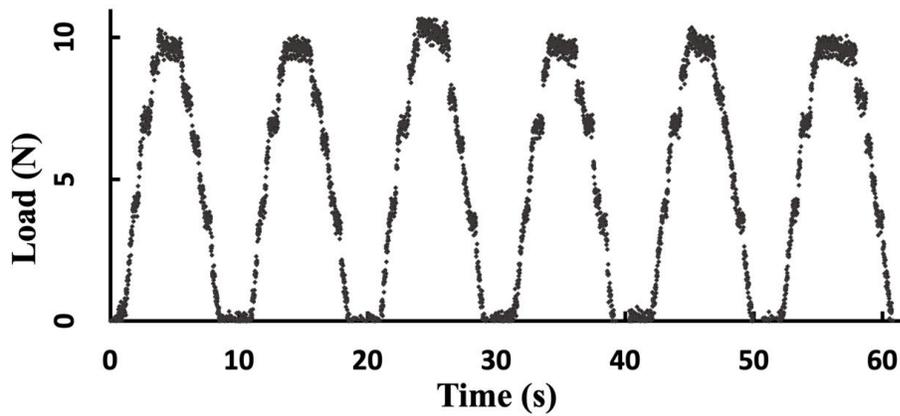


Figure 11. An applied triangular-wave tensile load of 0-10 N

Figure 12 presents the peak to peak voltage output vs the porosity of the PVDF sensors. One particularly interesting fact is that the voltage output increases from approximately 0.18 V to 0.83 V as the porosity increases from 0.0% to 23.7%, and then decreases to 0.24 V as the porosity further increases to 42.0%. The results proved that

the piezoelectric effect was enhanced with the increase of the porosity to 23.7% and then reduced with a further increase of the porosity to 42.0%, which is consistent with the change of the  $d_{31}$  value as discussed in Section 3.2. The results also suggested that the produced voltage from the sensors can easily be detected by a multimeter, which demonstrated their strong sensing effect on a small load.

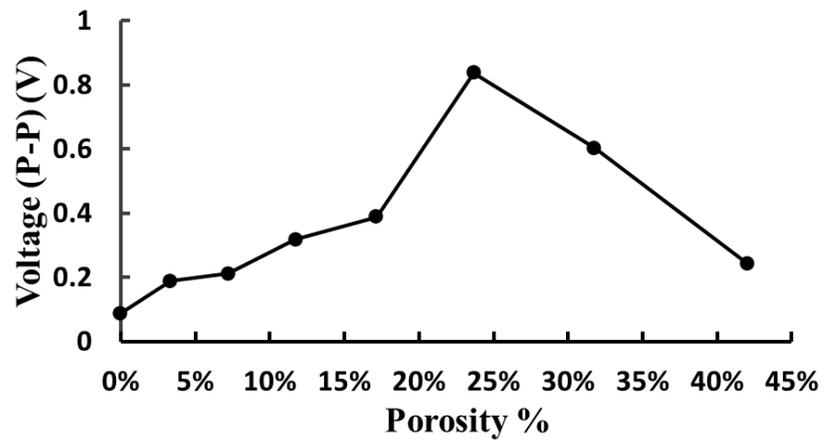


Figure 12. The piezoelectric coefficient  $d_{31}$  vs the porosity of the PVDF sensors

## CHAPTER IV CONCLUSIONS

In this research, a group of ZnO PVDF sensors have been successfully fabricated using nanoporous piezoelectric PVDF thin films. This type of sensor can generate considerable electrical potential by applied both static and dynamic loads. Compared to a pure PVDF film sensor, the nanoporous PVDF thin film sensor possesses several unique merits that are critical for developing measurable signal outputs to show reliable response. The PVDF sensors are extremely light and flexible and can be fabricated in small sizes. A considerable voltage output can be obtained when subjected to a small load.

Eight sets of samples with different ZnO amount that ranges from 0 to 70 wt.% were prepared, resulting in the corresponding porosities from 0 to 42%. The porosity effect on the sensor samples was studied under a tensile load and the piezoelectric coefficient  $d_{31}$  was characterized.

The results indicated that the piezoelectric coefficient  $d_{31}$  increased from 0 to 23.7%, and then decreased as the porosity increased to 42.0%. The PVDF sensor with 23.7% porosity exhibited the highest piezoelectric coefficient, suggesting the strongest piezoelectric effect.

Furthermore, the sensor's behavior under cyclic loading was investigated and the results indicated that the sensor could properly detect the dynamic load ranging from 0 to 10 N. The voltage output from the sensors also increased from 0 to 23.7%, and then decreased as the porosity increased to 42.0%. The optimal porosity value was determined as 23.7%, which agrees with the  $d_{31}$  value.

The study demonstrated that the porosity played an important role on the piezoelectric properties and sensing effect of the PVDF sensors. Adding nanoporous structures into the PVDF film was an effective approach to increase its piezoelectric effect because of the  $\beta$ -phase enhancement. The modified nanoporous PVDF film was very suitable for sensing applications.

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