Characterization of PZT/PVDF Composite Film as Functional Material

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Abstract—**In this paper, we obtained and characterized a composite film made of lead zirconate titanate (PZT) piezoelectric ceramic and nonpolar polyvinylidene fluoride (α-PVDF) as a functional material. The scanning electron microscopy results show this composite film to have mixed connectivity due to the agglomeration of some of the PZT particles. The response of the composite to an applied ac voltage at 4110 Hz has a slope of 0.074 nm/V. The measured displacement is in the range of 0–30 nm for electric voltages ranging from 0 to 400 V. The experimental results show the composite performance as an acoustic emission sensor to be in good agreement with the response of a commercial standard microphone in the frequency range of 2–6 kHz. By applying 2 kN of cyclic force at a frequency of 3 Hz, we obtained an 80-V peak signal and calculated a dissipated power equal to 158 μW.**

Index Terms—**Lead zirconate titanate (PZT), non-polar polyvinylidene fluoride (α-PVDF).**

I. INTRODUCTION

TODAY, functional materials are the target of much multidisciplinary research toward the development of a new material that can perform a number of specific engineering functions. Although Thomas [1] suggested that any material could be designated as functional, the goal here is to obtain a truly smart material, that can be used as both a sensor and actuator at the same time.

In this regard, several studies have been conducted and different kind of materials used, such as polymers, fiber composites, and metallic foams, depending on the application. The main objective is to integrate the actuation mechanism that controls the structural motion with the sensing mechanism that monitors the structure [2]–[6]. The number of papers on this subject has increased considerably with the growing interest in nanomaterials [7]–[9] and the corresponding range of applications.

Of the multifunctional materials, piezoelectric materials, i.e., piezoelectric ceramic and piezoelectric polymers, have important roles since they can function as both actuator and sensor materials. Several good papers published in the past decade have focused on their sensing and energy harvesting characteristics of them [10]–[14]. The study of piezoelectric materials has included ferroelectric polymers and copolymers and ferroelectric ceramics. However, for some specific applications, these may not work adequately due to their individual properties, such as the low dielectric constant in polymers and the mechanical fragility of ceramics. To overcome this problem, the ceramic/polymer composite has been developed as an alternative material that combines the properties of each single phase to yield a new material with a tailored performance as either actuating or sensing.

The use of piezoelectric materials instead of electromagnetic devices is in response to the advantages offered by piezo materials, including their suitability to miniaturization, no electromagnetic noise generation, and higher efficiency [15]. For two-phase composites consisting of an electroactive ceramic and polymer, according to Newnham *et al.* [16], the 0-3 connectivity pattern, i.e., “0” for the isolated ceramic particles dispersed into the “3” polymer matrix connected in all three dimensions, is the lowest in cost and easiest composite to produce of the ten possible combinations. Of course, depending on the ceramic fraction content in the composite, the sample can display a mixed connectivity (0-3 and 1-3) while maintaining its flexibility and ease of preparation.

The PZT/polymer composite has been extensively studied over the last three decades, with the main objective being improvement of the electromechanical properties of the new material. To do so, many polymer phases have been used as the matrix, in which the ceramic phase is dispersed to form the composite material. All PZT/polymer composites show increased piezoelectric activity as the ceramic content is increased. Also, the composite material has shown an enhanced piezoelectric coefficient when poled with a higher electric field [17]–[21].

Based on these results and because the focus of the present work is to demonstrate the potential of the PZT/PVDF composite film as a functional material, the results reported here are for a 50/50 vol% composite. The sample with a 30 vol% of PZT yielded a low piezoelectric coefficient and that with a 70 vol% of PZT was brittle and broke under an applied 2 kN force. Although we analyzed samples with only one PZT/PVDF ratio (50/50 vol%), the results of this study

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contribute to the sensor and actuator research area since they show that an PZT/PVDF composite sample can be used as an AE sensor, as an actuator that produces displacement in the nanometer range, and also as a renewable source to generate clean energy.

II. MATERIALS AND METHOD

We obtained circular PZT/PVDF composite films 50 mm in diameter, and 0.5 mm thick by hot pressing a mixture of PZT ($\rho = 7.6$ g/cm3) and α-PVDF ($\rho = 1.8$ g/cm3) powders. We purchased the PZT powder from American Piezo Ceramics (APC) under reference 850. Its characteristics include a: Curie temperature of 360 °C, relative dielectric constant equal to 1900 (1 kHz), average particle size of 50 μm, and piezoelectric charge constant d33 = 400 pC/N. We obtained the PVDF powder from Solvay, which, according to the manufacturer, has an average grain size of around 80 μm. We manually mixed the powder and placed the mixture on a Kapton sheet, which we then placed in a stainless-steel die. To produce the sample, we then pressed the die with the well-mixed powders at an empirically determined pressure of 2.4×10^7 Pa for 1.0 min at 190 °C, using a thermocouple to indicate the temperature. We selected the desired volume percentage of PZT and calculated the mass of the constituents using (1), as follows:

$$M_{PZT} = M_{PVDF} * \frac{\rho_{PZT}}{\rho_{PVDF}} * \frac{\%PZT}{1-\%PZT} \quad (1)$$

where, M is the mass, ρ is the density, and %PZT is the fraction of PZT in the composite sample.

To generate piezoelectric activity, based on [17], we poled the samples with a 10 MV/m electric field. We immersed the samples in silicone oil to prevent electrical breakdown performed poling for 1.0 h, while maintaining the poling temperature at 90 °C. To establish electrical contact, we vacuum evaporated aluminum electrodes onto both sides of each sample. A high-poling electric field is achieved due to the polymer phase in the composite film.

To characterize the PZT/PVDF 50/50 vol% composite film and determine the particle distribution in the polymer matrix, we used a JOEL model JSM-7500F scanning electron microscope (SEM-FEG). We used energy dispersive spectroscopy (EDS) to analyze the chemical components of the composite. Figure 1 shows a block diagram of the equipment used to analyze the performance of the composite as an actuator. The optical interferometer we used is based on that used in the Michelson experiment [22].

We investigated the acoustic emission detection properties of the PZT/PVDF composite film with reference to the American Society for Testing and Materials -ASTM E976-10 standard [23], as shown in Fig. 2. The pencil-lead break is a conventional and well-known test for the detection of acoustic emissions.

We also performed energy conversion tests on a system that simulates the pedestrian and automobile traffic on a track in which a composite film is embedded. To the sample, we applied a force of 2 kN at a cyclical frequency of 3 Hz and obtained the electrical signal by observing the sample deformation on an oscilloscope. In the energy harvesting experiment, we placed the sample between two copper thin foils, which served as the electrical contact. To protect the sample, we placed this system between two aluminum plates 2.0 mm thick. To simulate a street on which people walk or cars travel, this apparatus uses a steel roll driven by a planer machine to apply mechanical deformation force onto the composite film. The roll was boosted onto the sample with a 2 kN force at a frequency of 3 Hz and we used an oscilloscope to record the electrical signal generated by the sample (Agilent DSO6012A), as shown in Fig. 3.

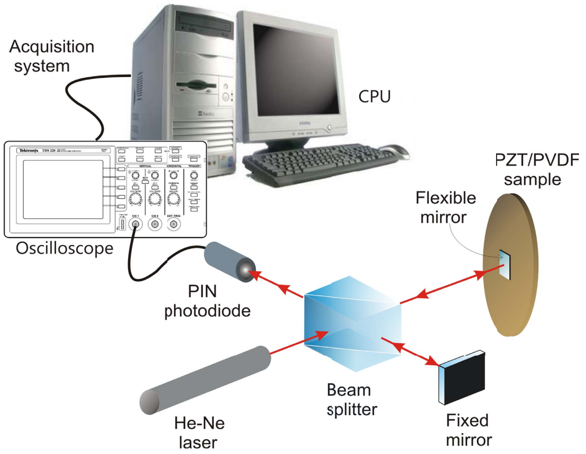

Fig. 1. Block diagram to analyze the actuator property of the composite sample.

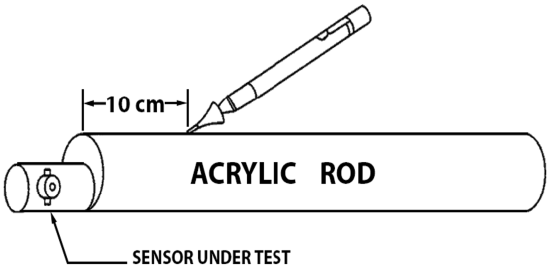

Fig. 2. Pencil-lead break test Hsu-Nielsen method.

III. RESULTS AND DISCUSSION

We analyzed a 50/50 vol% PZT/PVDF sample 50 mm in diameter and 0.5 mm thick using (2), which was proposed by Guo *et al.* [24]:

$$d_{33} = \frac{\kappa \varepsilon_0 A V_p}{F t} \quad (2)$$

where κ is the relative dielectric constant, $\varepsilon_0 = 8.85 \times 10^{-12}$ is the vacuum permittivity, A is the sample area, V_p is the peak voltage, F is the applied force, and t is the sample thickness. We obtained the value of 72 pC/N. The SEM results revealed the size of the PZT particles to range from 130-300 nm, dispersed throughout the PVDF matrix. In Fig. 4, we can see some agglomeratione of particles, which indicates mixed

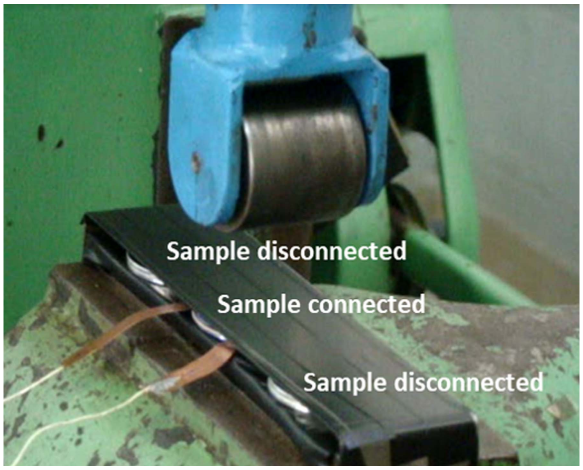

Fig. 3. Apparatus used to simulate car traffic on the composite sample to generate energy.

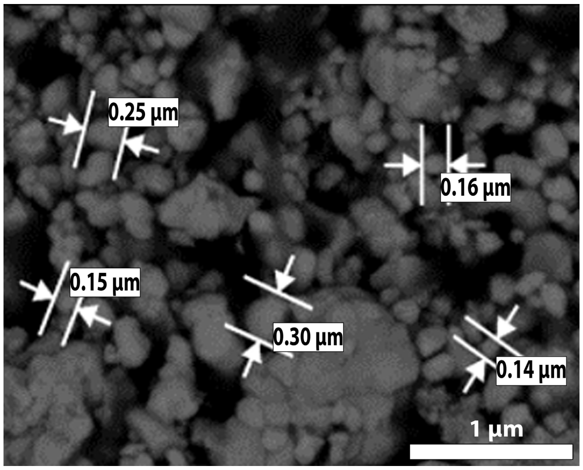

Fig. 4. Backscattering image of the fractured surface of PVDF/PZT composite.

connectivity. With 50 vol% of PZT, the composite cannot be considered to be a pure 0-3 composite, since there is some connection between particles. The EDS analyses (Fig. 5) showed no composite contamination or chemical reaction between the individual phases. We also observed the presence of carbon in the EDS spectrum of the composite film in the pure PZT spectrum, which was thought to be due to the ITO conductive tape used to fix the sample to the holder.

Figure 6 shows the actuator performance of the composite film. We observed a linear relationship between the mechanical displacement and the applied electrical voltage. The mechanical deformation of the composite film under the applied electrical voltage is related to the inverse piezoelectric effect of the poled PZT particles, since PVDF is non-polar. We used three different frequencies: 3100 Hz, 3600 Hz, and 4110 Hz. The slope indicates the calibration factor of the composite as an actuator, which depends on the frequency of the applied electrical signal. At 4110 Hz, the composite film displayed better sensitivity to deformation with 0.074 nm/V, followed by the response at 3600 Hz with 0.023 nm/V and finally the composite film at 3100 Hz with 0.015 nm/V. We observed a small hysteresis in the higher frequency (0.4 nm), as shown in Fig. 7.

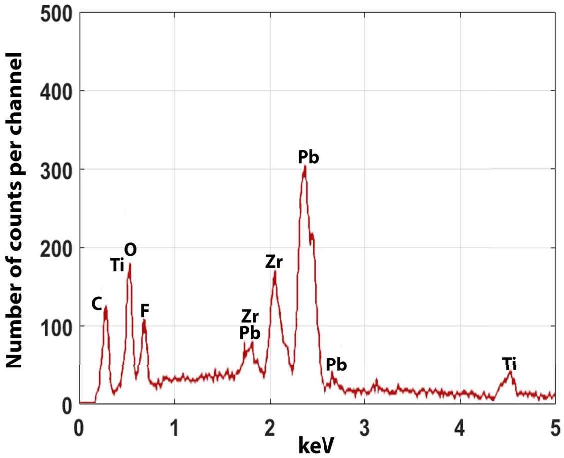

Fig. 5. EDS results for the PZT/PVDF sample.

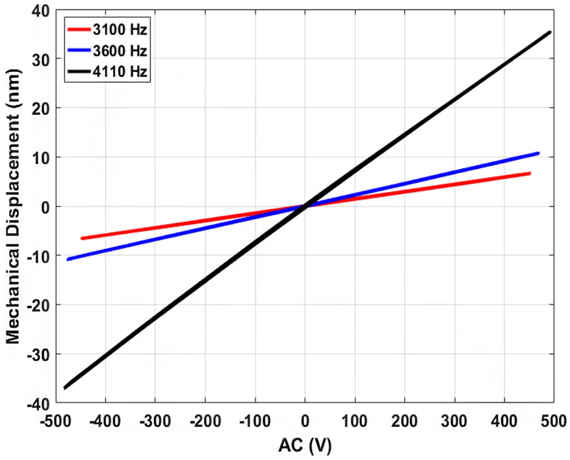

Fig. 6. Sample response to applied electric voltage.

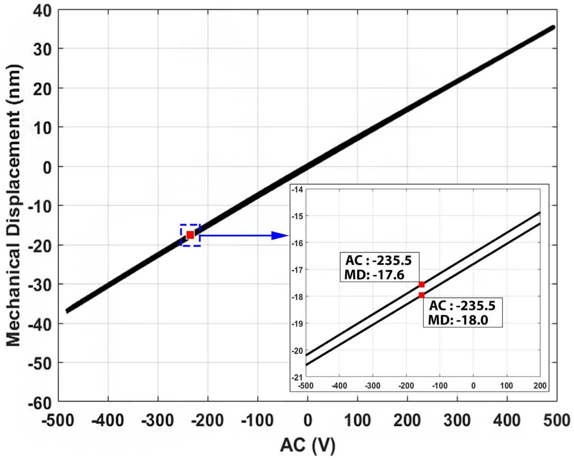

Fig. 7. Small hysteresis for 900 V peak-to-peak applied voltage.

To demonstrate the composites capacity for use as an acoustic emission detector, we performed a pencil-lead break experiment. In the experimental setup, shown in Fig. 2, we used the ASTM E 967-10 standard. Following the well-known Hsu-Nielsen experiment [25], we broke the pencil lead 10 cm from the sensor.

Figure 8 shows the sensor response as a function of time. In the test, we eliminated the DC component of the signal and

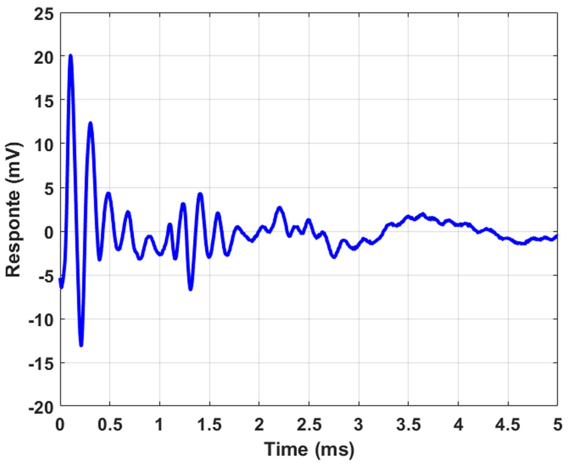

Fig. 8. AE Sensor response in the time domain.

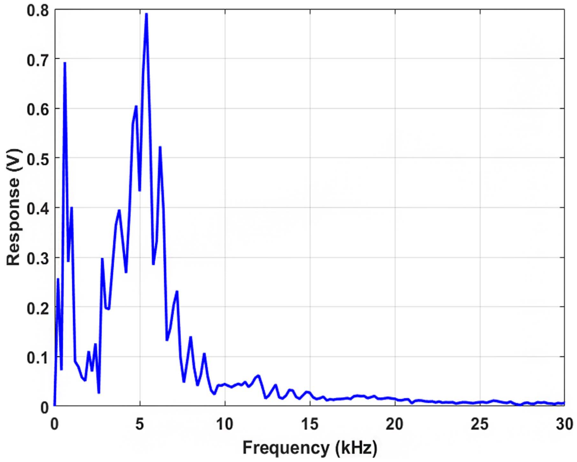

Fig. 9. AE Sensor response in the frequency domain.

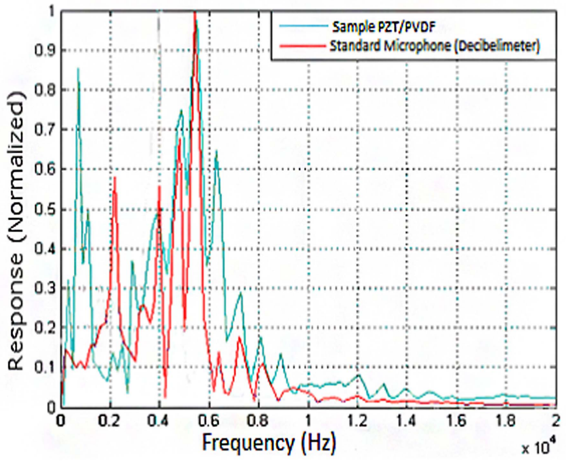

Fig. 10. Normalized response of the sensor for acoustic emission.

noise. Similar results were reported by Or *et al.* [26] for the P(VDF-TrFE) copolymer. The Fourier transform of the signal, shown in Fig. 9, has a maximum amplitude around 5 kHz.

To verify the quality and magnitude of the PZT/PVDF AE sensor, we compared its response to that of a standard microphone in the system shown in Fig. 2. As we can see in Fig. 10, there is good agreement in the responses of the sensors in the frequency range of 2-6 kHz.

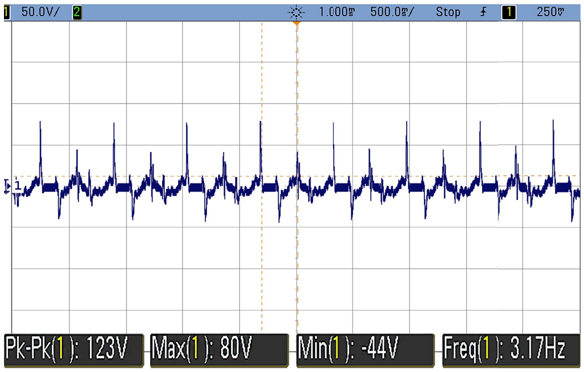

Fig. 11. Composite's response to the deformation produced by the steel roll.

Figure 11 shows the composite's response to the deformation produced by the steel roll. The roll moves forward and backward, thereby generating positive and negative peaks. The composite sample produced a peak signal value of 80 V. To calculate the dissipated power, we connected a resistive load of 100 kΩ to the sample and we measured an RMS voltage of 3.98 V, which provides 158.5 μW, which gives 1.6 μW/cm^3. Zhou *et al.* [27], using PZT nanowire found 2.4 μW/cm^3. We used a 100 kΩ resistor to consider the impedance match with the electrical circuit [28].

IV. CONCLUSIONS

In this study, we obtained mechanically resistant PZT/PVDF and flexible composite films with mixed connectivity. After the polarization process, we used the composite as both a sensor and actuator. The application of electrical signals with amplitudes in the range of 0-500 V produced mechanical displacements of the composite in the nanometer range. We observed a very small hysteresis (0.4 nm) following the application to the composite of an electrical signal with a frequency of 4110 Hz.

With regard to sensing, the composite showed sensitivity in detecting a sudden release of energy by a pencil-lead break 10 cm away from the sensor. This pencil-lead break test simulates certain structural failures, such as a crack inside a structure. The result obtained by the sensor indicates that it can be used as an acoustic emission sensor.

The results of the energy-harvesting experiment indicate a material that merits further careful study. There is real potential for using the described composite material as a renewable source to generate clean energy for electronic devices and battery charging.

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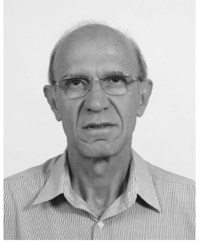

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