Piezo-Energetic composite film fabrication and poling process for pressure sensor applications

D. Messer[1]*, T. Hafner[1], M. Örnek[3], M. Paral[2], S. F. Son[13]

[1]School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, USA
[2]School of Aeronautics and Astronautics, Purdue University, West Lafayette, Indiana 47907, USA
[3]Purdue Energetic Research Center, West Lafayette, Indiana 47907, USA

*Corresponding author email: messer3@purdue.edu

ABSTRACT

Smart energetics refer to propellants, explosives, pyrotechnics, etc. that are capable of being manipulated through a wide variety of characteristics which can be toggled go or no-go, or those that have controllable energy levels. Therefore, the interest in the development of smart energetics has been on the rise. Initial research has been conducted on enhancing performance of energetic systems through their electromechanical properties such as piezoelectricity. Among polymers, fluoropolymers like poly(vinylidene fluoride) (PVDF) and its copolymers such as poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) have the highest piezoelectric coefficient. The use of PVDF as the binder and oxidizer and nano-aluminum (nAl) as the fuel in an energetic composite has been well established. However, there is limited research on the electromechanical properties of energetic composites. In this study, a piezo-energetic film was fabricated using nAl (10wt% active content) and PVDF-TrFE (70/30). The film was then poled and the piezoelectric response was tested using a small-scale drop-weight setup. The piezoelectric response was quantified for poled and unpoled nAl/PVDF-TrFE films. The piezo-energetic films replicated the behavior of a commercial pressure gauge, whereas the unpoled films had little to no response. The poling time and electric field were shown to have a positive correlation with the piezoelectric coefficient. The max d_{33} value was -12 pC/N for nAl/PVDF-TrFE compared to -24 pC/N for neat PVDF-TrFE. A piezoelectric response of this magnitude has not been reported before for energetic materials and can be useful for pressure sensor applications in the field of energetics and pyrotechnics.

INTRODUCTION

Two mechanisms that generate electric polarization are piezoelectricity and flexoelectricity. Piezoelectricity generates an electric polarization under a homogeneous strain whereas flexoelectricity is present under a strain gradient. This infers that piezoelectricity observes applications in mechanical impulses, pressure changes, or vibrations and flexoelectricity is most useful when bending or flexing [1,2][. Flexoelectricity is present in all dielectric materials so it cannot be ignored. However, piezoelectricity is more dominant in effecting polarization when present due to mechanical restrictions on forming large strain gradients [3]. Ferroelectric ceramics and lead-based piezoelectric single crystals are the piezoelectric materials with the highest piezoelectric coefficients [4,5]. This is because the electric polarization under a homogenous strain requires that the material be non-centrosymmetric. Among

polymers, fluoropolymers like poly(vinylidene fluoride) (PVDF) and its copolymers have the highest piezoelectric coefficient [6,7].

There are five different crystallographic phases that PVDF exists in: alpha (α), beta (β), and gamma (γ), delta (δ) and epsilon (ε). However, PVDF exhibits piezoelectric, pyroelectric, and ferroelectric properties at their strongest in β-phase [8]. Post-processing methods, such as mechanical stretching, drawing, or high temperature and pressure treatments have to be performed to achieve the desirable β-phase since PVDF naturally exists in the α-phase [9]. On the other hand, poly(vinylidene fluoride-trifluoroethylene) is a copolymer that naturally exhibits ferroelectricity due to the formation of a more thermodynamically stable β-phase caused by TrFE addition [10,11]. The films are rendered piezoelectric by applying an electric field which aligns the dipoles in a process called poling. The most widely used measurement to quantify the piezoelectric effect is the piezoelectric coefficient (d_{33}). The d33 constant characterizes the extent of the material's piezoelectricity and is around -32 pC/N for high-performing commercial films [12].

The simplest way to acquire an electrical signal delivered by a piezo film is through measurement in voltage mode [13]. This can be performed by a drop-weight setup and requires the user to convert the output to a piezoelectric coefficient. On the other hand, a berlincourt type d33 tester is already calibrated to output the coefficient. Because of the high response of the piezoelectric polymer, no power supply or amplifier is required to observe the signal. Advantages of using PVDF as a pressure sensor include direct measurement of impact pressure, short pulse duration, wide frequency range, high voltage output, and low cost to fabricate [14,15]. Combining this property with nano aluminum would create a multifunctional and "smart" energetic composite.

It is well established that PVDF and other fluoropolymers are effective oxidizers in energetic materials and novel combustion techniques are observed (impact, friction, and laser ignition) [16–18]. However, there has been limited research of the electromechanical properties in these energetic systems. Initial research was performed by Row and Groven by utilizing the piezoelectric effect to develop smart reactive materials that can have tunable performance or ON/OFF capabilities [19]. This research was expanded when Messer et al. reported on the correlation of impact ignition sensitivity and the piezoelectric coefficient of nAl/PVDF-TrFE composites [20]. Margevicius also attempted to sensitize these composites by manipulating the d_{33} value [21]. Her work displayed that the burn rate increased for piezoelectric nAl/PVDF-TrFE composite films when a voltage was applied to the sample whereas the unpoled samples displayed no change in burn rate. Still, the electromechanical response of energetic composites has not been fully explored.

The objective of this study is to demonstrate that PVDF used in an energetic composite film can retain its piezoelectric properties and perform the same applications. This was achieved by measuring the d_{33} value of nAl/PVDF-TrFE films and calibrating them to predict impact force. It should be noted that we only performed tests under the impact ignition threshold found in our previous work [20]. The piezo-energetic films were subject to a metal ball being dropped at various heights to produce different forces. The dynamic response of the films is observed using an oscilloscope. The output voltage is measured and converted into the impact force. The study followed a simple and proven method to measure impact force

from the samples. Therefore, it is proven that piezo-energetic composite films can be used as pressure sensors and expands the possibilities for future pyrotechnic applications.

EXPERIMENTAL SECTION

Materials. The P(VDF-TrFE) material used was a 70/30 Poly(VDF-co-TrFE) (Vinylidene Fluoride and Triflouroethylene Copolymer) powder purchased from Arkema. The nano aluminum was purchased from Novacentrix and was nominally 80nm in diameter. The nAl powders were 70% active as determined by differential scanning calorimetry and thermogravimetric analyzer (DSC/TGA) and shown in a future section. The dimethylformamide (DMF) was purchased from Acros Organics.

Fabrication and Characterization. The material fabrication process is similar to the one outlined in Messer et al [20]. The composite films are composed of 9 wt% nAl, or ~6 wt% active nAl. The nano aluminum and P(VDF-TrFE) were suspended in DMF at a ratio of 1 gram of solid to 5mL of DMF. First, the nAl/DMF mixture was mixed by a higher-energy ultrasonic mixer. The mixer (Branson) was run for 1.5 minutes on (15% ultrasonic amplitude), then 1.5 minutes off for a total of 6 minutes. Following the solution becoming homogenous, the P(VDF-TrFE) was added and the new mixture was sonicated for 1.5 minutes on (15% ultrasonic amplitude) and 1.5 minutes off for a total of 9 minutes. After the solutions were well mixed, a tape caster (MSK-AFA-HC100, MIT) was used to create films with uniform thickness and nearly full density. The tape caster was run with a bed set at 95 °C and a blade height of 1 mm. After the blade glided across the solution, the film rested on the heating bed for 15 minutes to dry. The resulting average thickness of the casted film was 25-30 μm. The fabrication process as well as the final composite film can be seen in Fig. 1.
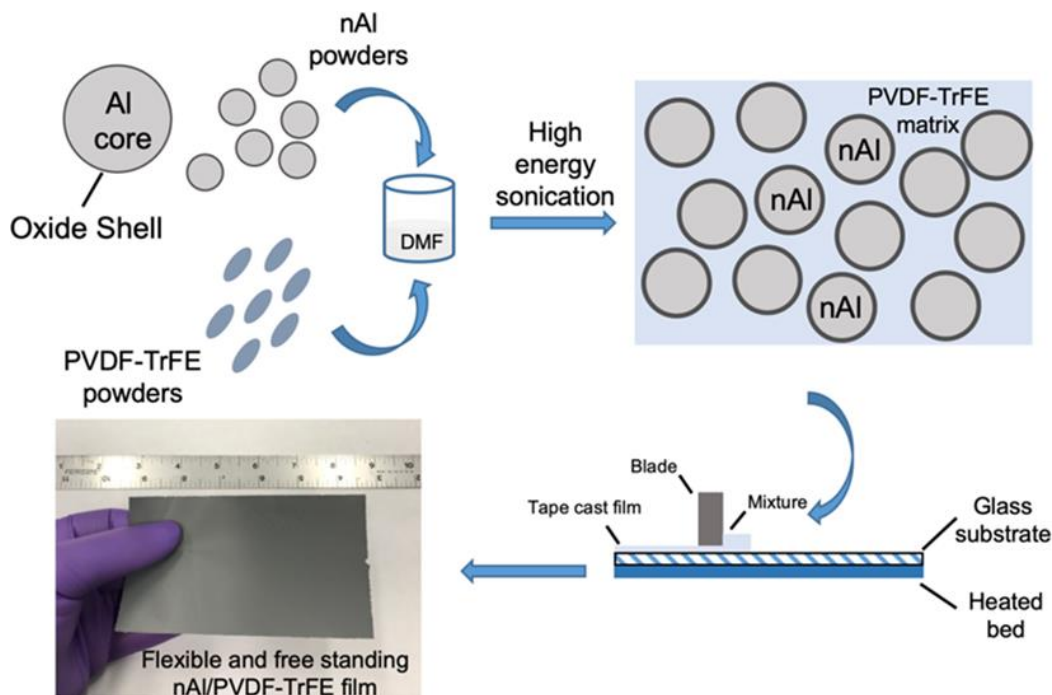

Figure 1. Film fabrication process

Poling. The poling process outlined in Messer et al. [20] was used for this work. The films were placed in between two Indium tin oxide (ITO) glass slides (MSE Supplies). The ITO slides had conductive surfaces that were used as the electrodes in the poling process. A neat glass slide was placed above the film and below the top electrode slide as a protection against electrical breakdown and ignition of the composite film. This 1 mm dielectric barrier and 28 µm film were used when calculating the electric field from the applied voltage. Figure 2 below is a schematic of the poling setup. The poling assembly was resting on top of a hot plate and held constant at 70 degrees celsius. The purpose of the hot plate was ato crystalize the PVDF-Trfe by heating to a point above the Curie point and below the melting point. The ITO glass electrodes were connected to a high voltage power supply (ET40, Glassman). A voltage range of 5 kV to 20 kV was applied to the film to achieve the materials' optimal d_{33} value. A Berlincourt type piezoelectric tester (PolyK Technologies) was used to measure the d_{33} value and quantify the success of the poling process. Poling nAl/P(VDF-TrFE) proved much more difficult than neat P(VDF-TrFE), achieving lower piezoelectric coefficients at the same applied electric field. The electric field was held constant for two minutes. Piezoelectricity was not shown to increase for a longer time than this.

Figure 2. Poling schematic.

Calibration Method. A drop weight setup was created in order to measure the voltage response from films after being impacted with a force, or pressure. A 66.7g metal ball was used to drop onto a round metal plate, with a 20 cm^2 impact surface, which then compresses the sample. A clear PVC pipe was used to guide the metal ball to ensure repeatable tests. The sample film was given a top and bottom electrode to transport the signal generated from impact. For the electrodes, nickel on copper-plated polyester tape (2191FR) from The 3M Company was used. The two leads were attached to wires directly connected to the oscilloscope where it is recorded. Figure 3 is a schematic showing the setup. The drop height was varied from 1 to 4 inches for a total of four different drop heights. The drop height was used to easily visualize the correlation with voltage response; however, impact force and pressure were also calculated and the relationship to voltage output was observed. The max voltage was extracted from the data and was the only number used for quantitative analysis. The time history from the signal can also be observed to find the rise-to-peak time and decay time. This procedure is to demonstrate the use of the composite film as a pressure gauge.
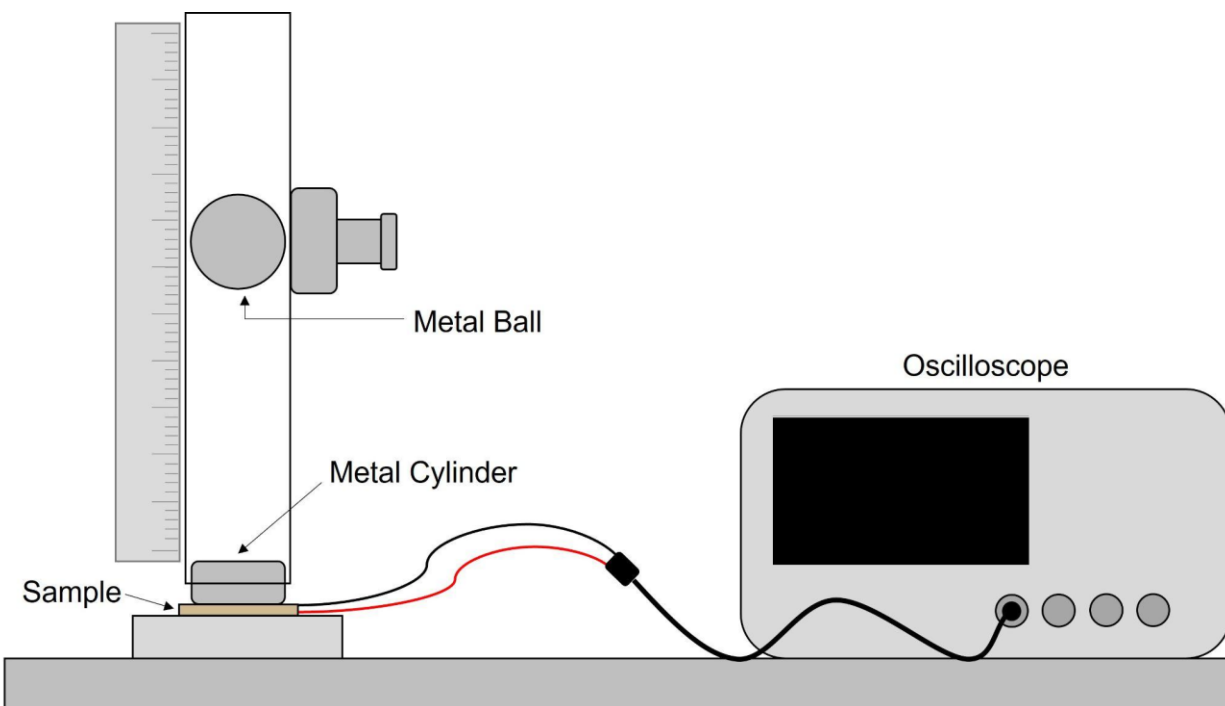
Figure 3. Schematic of mini drop weight.

RESULTS AND DISCUSSIONS

Film Characterization. Applying the manufacturing process outlined previously, P(VDF-TrFE) and nAl/P(VDF-TrFE) films of 28 ± 0.5 μm were fabricated. Previous work utilized Fourier-transform infrared spectroscopy (FTIR) scans to identify the electroactive phases and their possible changes in the P(VDF-TrFE) before and after nAl addition [ref]. It was determined that β-phase was retained in the material after nAl addition, indicating that the films can exhibit piezoelectricity via poling. Also, porosity was minimized in the manufacturing process. The porosity of the films is controlled by the temperature of the tape caster bed during casting. By raising the temperature of the drying bed, the DMF is evaporated out of the films at a more rapid pace and allows for the liquid mixture of P(VDF-TrFE)/nAl to form films with higher density. A drying temperature of 125 °C was found to consistently result in minimal porosity and was used to prepare the full density sample for solids loading experiments. This was also confirmed with an Archimedes density tester using the buoyancy technique. The results showed that the composite film was 97% of theoretical maximum density (TMD).
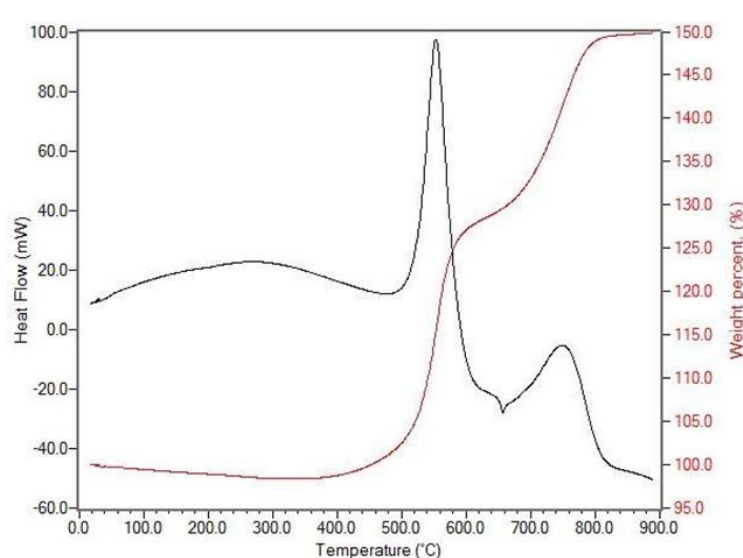
Figure 4. Thermal Analysis from DSC/TGA.

The thermal analysis shows that the onset temperature does occur around 500 °C as expected. Figure 4 was extracted from DSC/TGA which measured heat flow and weight percent of nAl. The temperature was set at a constant rate of 10 °C every 5 minutes after rapidly being increased to 300 °C. As the nano aluminum is oxidized the mass increases to about 157% of its original weight. The mass of Al and Al2O3 is 27 and 102 grams respectively. The mass increase from 2 moles of aluminum to one mole of aluminum oxide is 188%. In this scenario the aluminum would be one hundred percent active, but our weight increase was found to be less. Comparing the stoichiometric and actual values, it can be concluded that the nano aluminum used was 67% active.

Poling Study on the Strength of the Electrical Field. An investigation into the effect of the magnitude of the electrical field on the results of the poling process was conducted. Five samples were tested at applied voltages between 5 and 20 kV with increments of 2.5 kV. It can be seen in Fig. 5 that as the electrical field is increased the resultant d_{33} value increases. The poling process was rendered ineffective below an electric field of 5 V/μm. Also, the material reached its max d_{33} value around 20 V/μm. The amount of time the samples were exposed to an electric field was 2 minutes. The same method of poling was less effective on P(VDF-TrFE) films with the addition of nAl. Electrical breakdown occurred around 20 V/μm with the current setup so no tests could be complete above this value.

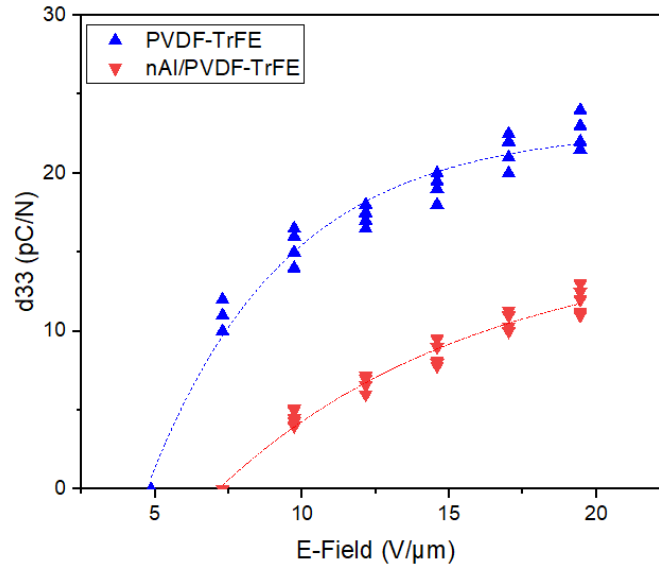**Figure 5**. d_{33} as a function of the electric field applied.

Calibration Curve. Figure 6 is an example voltage response as a function of time plot from the drop weight experiment for nAl/P(VDF-TrFE). The max voltage from these curves were extrapolated to quantify the electromechanical response at each drop height. The poled films experienced similar behavior which was a quick rise to the peak and a quick decline below zero before leveling out. The time-to-peak, or response time, was about 80 µs for each impact. The peak represents the quantifiable piezoelectric response from impact. For the unpoled films, this value was about zero for every height as expected. The value for the poled films increased with an increase in height and piezoelectric coefficient. The voltage dip below zero and leveling out can be attributed to the steel ball bouncing back up and releasing pressure off the sample. The resulting impact duration would be 2 ± 0.2 ms.
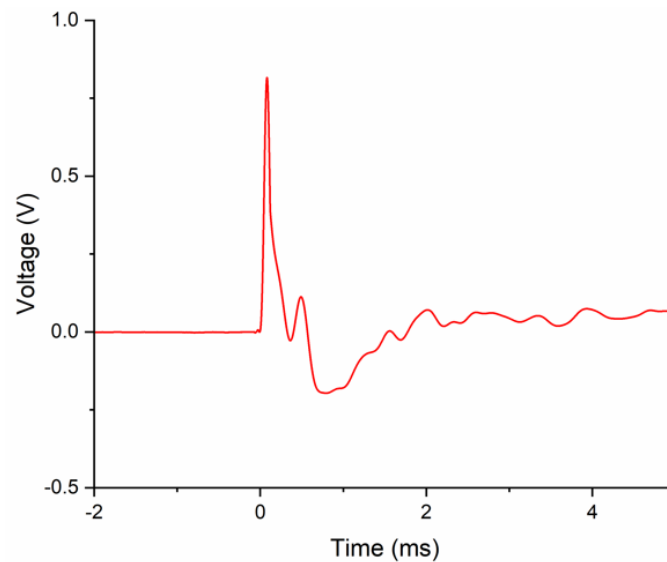

Figure 6. Voltage response as a function of time for nAl/PVDF-TrFE films. (a) poled (d_{33} = 12 pC/N) and (b) unpoled at a height of 2 inches.

The trend shown in both Fig. 7 and Fig. 8 is that increasing the d_{33} value increases the voltage, or piezoelectric, response of the film. As expected, the voltage response increases twice as much when the d_{33} value is doubled from 12 to 24 pC/N. Also, an increase in the drop height linearly increases the voltage response for the range of 1 to 4 inches. It should be noted that no calibration was made outside of this range. The d_{33} constant is simply a quantification of piezoelectricity in the units of charge per force. Therefore, the first trend matches the theory because for the same amount of force (same drop height), increasing the d_{33} constant will increase the charge output (voltage reading). For the 0 pc/N films, the voltage output stays the same as drop height increases. There are a few outliers at lower drop heights; however, the voltage observed could be caused by mechanical interference and not piezoelectric response. It was expected that the films with no piezoelectric coefficient would produce no voltage signal. The addition of nAl to the P(VDF-TrFE) films decreased the voltage response even though the d_{33} value measured from the berlincourt tester was the same.
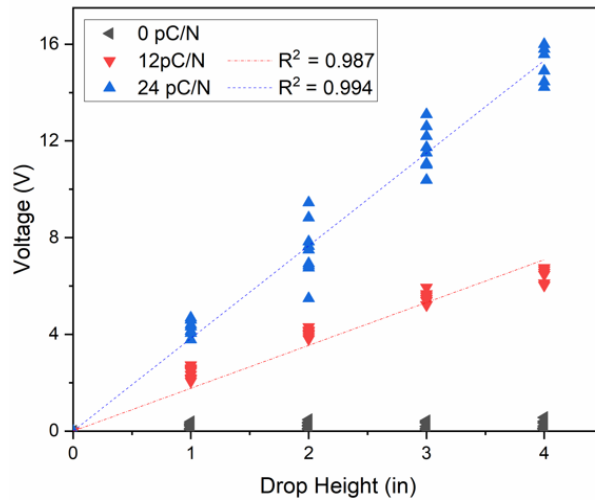

Figure 7. Voltage output as a function of drop height for four different P(VDF-TrFE) films.
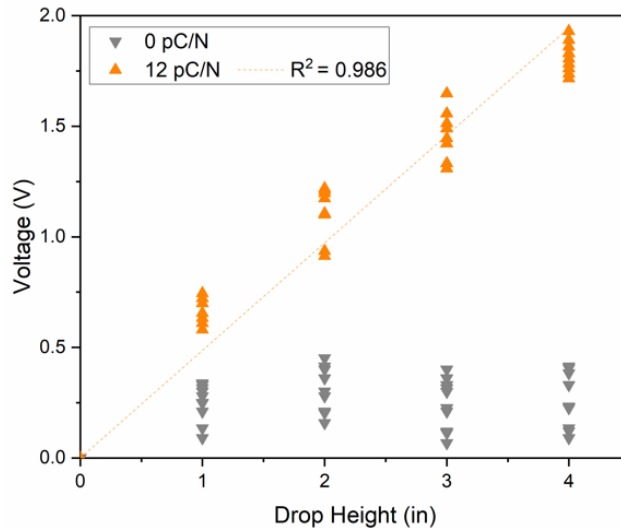

Figure 8. Voltage output as a function of drop height for two different nAl/P(VDF-TrFE) films.

To measure impact force, the following equation was utilized:

$$F_{imp} = \frac{m(v_1 + v_2)}{T},$$ (1)

where T is the impact duration, v_1 is the initial velocity of the ball, v_2 is the final velocity of the ball after the rebound and m is the mass of the ball. The coefficient of restriction is defined as $e = \frac{v_2}{v_1} = \sqrt{\frac{h_2}{h_1}}$ where h_1 is the drop height of the ball and h_2 is the rebound height of the ball. An energy balance can be done to acquire $v_1 = \sqrt{2gh_1}$. Equation 1 is updated with this information to obtain

$$F_{imp} = \frac{m(1 + e)\sqrt{2gh_1}}{T}.$$ (2)

Equation 2 is similarly used in other drop weight studies such as the one from Grinspan et al [14]. A video was taken of the ball drop to find the e and h_1. The impact duration used for all heights was 2 ms and was found via the oscilloscope data taken during the experiments. After testing several times, e is found to be approximately 0.35. The impact force for heights 1 through 4 inches were 31.8, 44.9, 55, and 63.5 Newtons respectively. These values along with the impact area were used to calculate pressure as seen in Fig. 9. Here, a calibration curve for a nAl/P(VDF-TrFE) is plotted to show the relationship between voltage output and pressure. The pressure can be calculated by using P = 18.70*V. This linear relationship is created so the composite film can be used as a pressure gauge with only an oscilloscope.
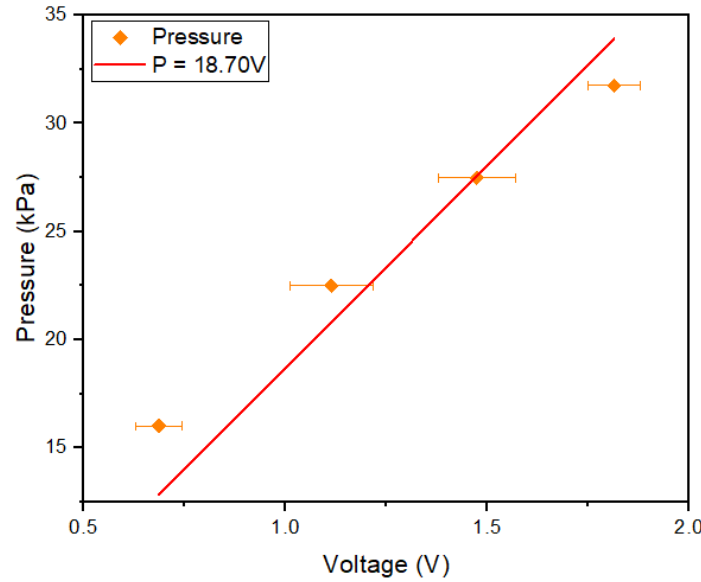

Figure 9. Relationship between voltage and pressure for poled nAl/PVDF-TrFE film

4. CONCLUSION

In summary, fluoropolymer films were created out of P(VDF-TrFE) and nAl. These films were then poled using a direct contact poling method. It was found that using a higher magnitude of the electrical field increased the d_{33} value of the poled films. The films were then subjected to a mini drop weight experiment and the voltage experiment upon impact was recorded. It was found that films with higher d_{33} values, gave larger voltage responses. It was additionally found that drop weight experiments conducted from a higher drop height supplied higher voltage response. Future work will include a study correlating the nAl content in the film to the electromechanical response. The oxide layer surrounding the nano-aluminum particles could be increased to prevent dielectric breakdown at higher applied electric fields.

References

[1]   A.K. Tagantsev, Piezoelectricity and flexoelectricity in crystalline dielectrics, Phys. Rev. B. 34 (1986) 5883–5889. https://doi.org/10.1103/PhysRevB.34.5883.

[2]   A.K. Tagantsev, Electric polarization in crystals and its response to thermal and elastic perturbations, Phase Transitions. 35 (1991) 119–203. https://doi.org/10.1080/01411599108213201.

[3]   T.D. Nguyen, S. Mao, Y.W. Yeh, P.K. Purohit, M.C. McAlpine, Nanoscale flexoelectricity, Adv. Mater. 25 (2013) 946–974. https://doi.org/10.1002/adma.201203852.

[4]   D. Damjanovic, Contributions to the piezoelectric effect in ferroelectric single crystals and ceramics, J. Am. Ceram. Soc. 88 (2005) 2663–2676. https://doi.org/10.1111/j.1551-2916.2005.00671.x.

[5]   S. Bauer, F. Bauer, Piezoelectric Polymers and Their Applications, Springer Ser. Mater. Sci. 114 (2008) 157–177. https://doi.org/10.1007/978-3-540-68683-5_6.

[6]   N. An, H. Liu, Y. Ding, M. Zhang, Y. Tang, Preparation and electroactive properties of a PVDF/nano-TiO 2 composite film, Appl. Surf. Sci. 257 (2011) 3831–3835. https://doi.org/10.1016/j.apsusc.2010.12.076.

[7]   A. V. Shirinov, W.K. Schomburg, Pressure sensor from a PVDF film, Sensors Actuators, A Phys. 142 (2008) 48–55. https://doi.org/10.1016/j.sna.2007.04.002.

[8]   L. Ruan, X. Yao, Y. Chang, L. Zhou, G. Qin, X. Zhang, Properties and applications of the β phase poly(vinylidene fluoride), Polymers (Basel). 10 (2018) 1–27. https://doi.org/10.3390/polym10030228.

[9]   P. Martins, A.C. Lopes, S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, Prog. Polym. Sci. 39 (2014) 683–706. https://doi.org/10.1016/j.progpolymsci.2013.07.006.

[10]   T. Sharma, S.S. Je, B. Gill, J.X.J. Zhang, Patterning piezoelectric thin film PVDF-TrFE based pressure sensor for catheter application, Sensors Actuators, A Phys. 177 (2012) 87–92. https://doi.org/10.1016/j.sna.2011.08.019.

[11]   Y. Li, C. Liao, S.C. Tjong, Electrospun polyvinylidene fluoride-based fibrous scaffolds with piezoelectric characteristics for bone and neural tissue engineering, Nanomaterials. 9 (2019). https://doi.org/10.3390/nano9070952.

[12]   E. Fukada, History and Recent Progress in Piezoelectric Polymers, Ieee Trans. Ultrason. Ferroelectr. Freq. Control. 47 (2000).

[13]   P. Ueberschlag, PVDF piezoelectric polymer, Sens. Rev. 21 (2001) 118–125.

[14]   A. Sahaya Grinspan, R. Gnanamoorthy, Impact force of low velocity liquid droplets measured using piezoelectric PVDF film, Colloids Surfaces A Physicochem. Eng. Asp. 356 (2010) 162–168. https://doi.org/10.1016/j.colsurfa.2010.01.005.

[15]   M. Toda, J. Dahl, PVDF corrugated transducer for ultrasonic ranging sensor, Sensors Actuators, A Phys. 134 (2007) 427–435. https://doi.org/10.1016/j.sna.2006.07.018.

[16]   S. Huang, S. Hong, Y. Su, Y. Jiang, S. Fukushima, T.M. Gill, N.E.D. Yilmaz, S. Tiwari, K. ichi Nomura, R.K. Kalia, A. Nakano, F. Shimojo, P. Vashishta, M. Chen, X. Zheng, Enhancing combustion performance of nano-Al/PVDF composites with β-PVDF, Combust. Flame. 219 (2020) 467–477. https://doi.org/10.1016/j.combustflame.2020.06.011.

[17]   K.E. Uhlenhake, D. Olsen, M. Gomez, M. Örnek, M. Zhou, S.F. Son, Photoflash and laser ignition of full density nano-aluminum PVDF films, Combust. Flame. 233 (2021) 111570. https://doi.org/10.1016/j.combustflame.2021.111570.

[18]   M. Örnek, K.E. Uhlenhake, Y. Zhou, B. Zhang, M. Kalaswad, D.N. Collard, H. Wang, Q. Wang, S.F. Son, Preparation and characterization of multifunctional piezoenergetic polyvinylidene fluoride/aluminum nanocomposite films, J. Appl. Phys. 131 (2022). https://doi.org/10.1063/5.0076258.

[19]   S.L. Row, L.J. Groven, Smart Energetics : Sensitization of the Aluminum-Fluoropolymer Reactive System, 1700409 (2018) 1–7. https://doi.org/10.1002/adem.201700409.

[20]   D. Messer, ALTERING THE IMPACT-DRIVEN SENSITIVITY AND IGNITION OF PVDF- TrFE/nAL COMPOSITES WITH PIEZOELECTRICITY, (2021).

[21]   M. Margevicius, Sensitizing Energetic Materials Using Piezoelectricity, (2019).