

**ALTERING THE IMPACT-DRIVEN SENSITIVITY AND IGNITION OF PVDF-
TrFE/nAL COMPOSITES WITH PIEZOELECTRICITY**

by

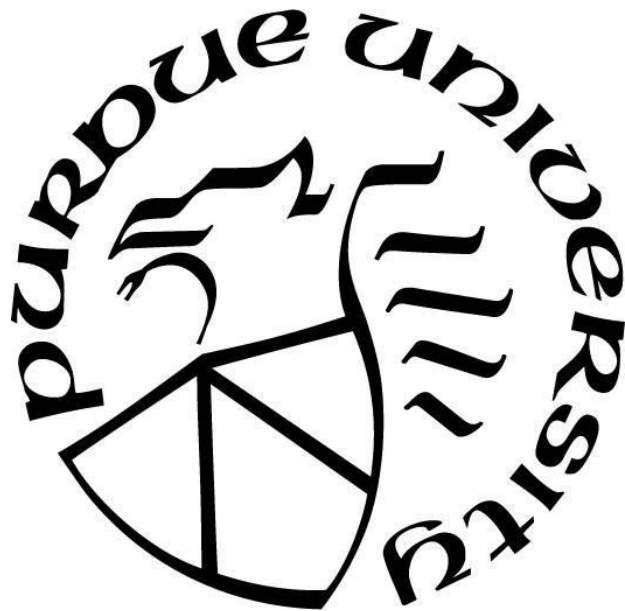
Derek K Messer

A Thesis

Submitted to the Faculty of Purdue University

In Partial Fulfillment of the Requirements for the degree of

Master of Science in Aeronautical and Astronautical Engineering



School of Aeronautical and Astronautical Engineering

West Lafayette, Indiana

August 2021

THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF COMMITTEE APPROVAL

Dr. Steven F. Son, Chair

School of Mechanical Engineering

Dr. Metin Örnek, Member

School of Mechanical Engineering

Dr. Christopher S. Goldenstein, Member

School of Mechanical Engineering

Dr. Sally P. M. Bane, Member

School of Aeronautics and Astronautics

Approved by:

Dr. Gregory A. Blaisdell

ACKNOWLEDGEMENTS

First of all, I'd like to thank my collaborators at Georgia Tech University for their modeling work. Credit for the figures in this section goes to Ju Hwan (Jay) Shin and Dr. Min Zhou. Also, my co-workers and friends made along the way played a major role in my success in and out of the lab. I'd like to thank Thomas Hafner, Kyle Uhlenhake, Ryan Merrell, and Mark Paral for helping me more than I asked for. Finally, I could not have accomplished so much without my biggest mentors pushing me. Dr. Metin Örnek has always made himself available to answer my calls for help. My advisor, Dr. Steven Son always kept an open door for anything from personal issues to new ideas around the lab.

This research was sponsored by the Air Force Office of Scientific Research Award No: FA9550-19-1-0008. Any opinions, findings, conclusions, or recommendations expressed in the article are those of the authors and do not necessarily reflect the views of the United States Air Force.

TABLE OF CONTENTS

LIST OF FIGURES	6
ABSTRACT.....	7
1. INTRODUCTION	8
1.1 Research Objectives.....	8
1.2 Method of Approach	9
2. BACKGROUND	10
2.1 Aluminum	10
2.2 Smart Energetics	11
2.3 Properties of PVDF.....	13
2.4 Application to Current Work	14
3. EXPERIMENTAL METHODS	16
3.1 Formulation Process.....	16
3.2 Poling Process	17
3.3 Characterization of Films.....	19
3.4 Sensitivity Tests	20
3.5 Ignition Delay Tests	22
4. MODELING	24
4.1 Microstructure Set-up	24
4.2 Governing Equations	25
4.3 Model Prediction.....	26
5. FILM CHARACTERIZATION	31
5.1 SEM Imaging	31
5.2 FTIR Analysis.....	32
5.3 Piezoelectric Coefficient Measurement	33
5.4 DSC/TGA Analysis	33
6. IMPACT TESTS	34
6.1 Sensitivity Test.....	34
6.2 Ignition Delay Test	34

7. SUMMARY AND CONCLUSIONS	37
7.1 Conclusion	37
7.2 Future Work	37
REFERENCES	39

LIST OF FIGURES

Figure 2.1. The molecular structure of PVDF and its phases [15] Error! Bookmark not defined.	
Figure 2.2. The experimental setup for Row and Groven's experiment [7]	13
Figure 3.1. Process for film fabrication	16
Figure 3.2. Tape caster	17
Figure 3.3. Schematic for poling set-up for thin films.....	18
Figure 3.4. High voltage power supply (left) and poling setup (right) used in experiment.....	18
Figure 3.5. Berlincourt type piezometer	19
Figure 3.6. Example of DSC/TGA for a typical nanoaluminum powder [25]	20
Figure 3.7. Two examples of a sample classified as a go	21
Figure 3.8. Schematic of Experimental Set-up	22
Figure 3.9. Example experimental output for unpoled film at 40 cm.....	23
Figure 4.1. A schematic illustration of the mechanical and electrical boundary conditions for the particle/binder composite model. The microstructure has a particle volume fraction of $\eta = 9\%$.	24
Figure 4.2 The distributions of induced electric potential and electric field within (a-b) a poled and (c-d) an unpoled film for the microstructure. The deformation corresponds to a drop-height of $h_0 = 20$ cm at $t = 109 \mu s$	27
Figure 4.3. An inset view of the electromechanical responses in the poled film near the particles at $t = 109 \mu s$ for $h_0 = 20$ cm. (a) normal stress along the y-direction (b) shear strain gradient (c) piezoelectric polarization along the y-direction (d) flexoelectric polarization along the y-direction (e) electric displacement magnitude (f) electric field magnitude	28
Figure 4.4. Evolution of the electric field magnitude within the poled binder for $h_0 = 20$ cm.....	29
Figure 5.1. Figure 5.1. SEM images of nAl/PVDF-Trfe with a side view (a)(d) and a zoomed in view (b)(d). Close-ups show a case with nAl agglomerated (c) and nAl particles dispersed within the fibrous PVDF-TrFE	31
Figure 5.2. FTIR of neat PVDF-TrFE and 10wt% Al in composite film	32
Figure 5.3. DSC/TGA of nAl.....	33
Figure 6.1. Cumulative Distribution Function of sensitivity of films.....	34
Figure 6.2. Ignition event caught by phantom v2012 camera.....	35
Figure 6.3. Comparison of thresholds showing the predicted time-to-PIR (dashed lines) and the experimental time-to-ignition (solid lines) for poled and unpoled films.....	36

ABSTRACT

Throughout the last century, energetic materials have been subject to drop weight impact tests to measure their sensitivity, with which material's properties are correlated to their impact sensitivity. However, there is little research that focuses on utilizing the piezoelectric effect to control the sensitivity of energetics. Piezoelectricity is the effect of an electric charge accumulating due to an applied mechanical stress. It is demonstrated in previous work that fluoropolymers such as polyvinylidene fluoride (PVDF) contribute to higher sensitivity in nanocomposite energetic materials through their piezoelectric properties. This property can be amplified in fluoropolymers in the beta (β) phase through polling methods and can be quantitatively analyzed by the piezoelectric coefficient (d_{33}). This research is focused on characterizing the effect of piezoelectricity on the impact sensitivity and ignition delay of nAl/PVDF-TrFE composites through the presence of varied d_{33} coefficients. The composite films were fabricated with the tape casting method with 85 μm thickness. The content of nAl was limited to 10 wt% in order to sustain feasible poling. Poling was achieved without any further manipulation of the composition so that a direct comparison could be observed. The magnitude of effect that the piezoelectric coefficient has on an energetic composite was discovered. The samples that had no d_{33} value were 8% less sensitive and experienced longer ignition delay times compared to the poled samples. This work proved that impact sensitivity and ignition delay can be manipulated through poling methods. This concept of controlling the sensitivity of energetic materials can be used to develop more customizable composites in the future.

1. INTRODUCTION

Optimization of energetic materials is important for safety and performance by ensuring desired behavior. This behavior is analyzed with sensitivity tests which include thermal, friction, impact, and electrostatic. The performance of energetic materials is limited by the potential energy and thermodynamics of the material. However, energetic materials can still be controlled through sensitivity and reactivity rather than energy release. Sensitivity can be controlled by manipulating nanocomposite energetic materials. When we use certain fluoropolymers with a fuel to create energetics that retain the advantageous properties of the dielectric material in the composite. One of these properties is piezoelectricity, which is the ability to generate charge against an applied mechanical impulse or vice versa. The piezoelectric effect can be altered through a method called poling. This process increases the piezoelectric coefficient of the material and thereby increases the electric response to an applied force. If the electric response is large enough, then a dielectric breakdown could occur and affect ignition behavior. The energetic material of choice will be subject to impact force in order to quantify this effect.

1.1 Research Objectives

The objective of this thesis was to develop a method for testing the sensitivity of an energetic material which is given the piezoelectric effect. The material's properties are evaluated to determine if they cause changes in combustion behavior. This objective was met by finding a useable material for a piezoenergetic, formulating the material, and characterizing the material electrically and experimentally.

- The first objective was to create a composite energetic material from PVDF-TrFE and nanoaluminum that can be poled and exhibit piezoelectric behavior.
- The second objective was to investigate the drop-weight impact sensitivity of poled and unpoled materials to elucidate the piezoelectric effect on the ignition sensitivity of the material.
- The third objective was to model the charge generation behavior caused by piezoelectricity and/or flexoelectricity

- The fourth and final objective was to investigate the ignition sensitivity of nAl/PVDF-TrFE films by modeling to better understand the mechanisms contributing to the ignition of this film.

1.2 Method of Approach

Formulation characterization of the piezoenergetics was built on previous research and was based on the available cost, time, and equipment. Nanoaluminum and PVDF-TrFE powders were purchased from reputable companies and were used in the experiments. The films were fabricated at Zucrow labs and were sufficiently completed with the equipment in the propulsion building. The thin films were able to be poled using a conventional setup with only a high-power supply and ITO glass slides as electrodes. The films did not have to be manipulated to achieve this so that a direct comparison could be done. Equipment used for characterization were located primarily in Flex lab in areas encompassed within the Purdue Energetics Research Center (PERC). SEM images were taken to ensure films were close to full density. FTIR spectroscopy was analyzed to ensure the composite films included enough beta phase for feasible poling. The experiments used a drop-weight apparatus that had multiple fall hammers available, but only 5kg was used to ensure every applied impact force is consistent.

The experimental procedure followed for the impact sensitivity tests was the Neyer D-Optimal test which is a modified version of the Bruceton up-and-down method. Here, the stimulus levels are determined through a more statistical approach rather than using consistent increments. This allows for a more accurate prediction of the L50 value. The test was complete under the condition that the standard of deviation went unchanged for five samples in a row. This led to significantly more samples than 25 recommended from the military standard (MIL-STD-1751A). The experimental data were compared with computational modeling performed at Georgia Tech University. The simulation analysis was implemented using COMSOL Multiphysics. This predicted the dielectric breakdown of the sample at a given time. Combustion mechanism was not calculated, but a direct comparison between ignition time and breakdown time was made.

2. BACKGROUND

2.1 Aluminum/ Fluoropolymer Systems as Energetic Materials

Aluminum is a popular fuel because it is low cost, non-toxic, and has a high specific gravity [1-3]. Aluminum particles are covered with a passivating oxide layer when exposed to the ambient atmosphere or oxidizing agents, and when this coating is destroyed, the aluminum ignites in an oxidizing atmosphere. Fluorine is very effective in reducing this oxide layer, as it is an even stronger oxidizer and removes and replaces the oxygen. The combustion of aluminum is significantly altered through particle size and changes in pressure and temperature [4]. This behavior is also shown in the combustion of aluminum in liquid water, as it changes with particle size, pressure, and oxide layer [5]. Research has been done on nanoscale aluminum combustion paired with various oxidizers, which manipulate the exothermic reaction that occurs [6]. The combustion of aluminum generates a condensed-phase product, and it has been difficult to determine the many details of aluminum combustion [7]. These difficulties are due to the size of combustion using nanosized particles and repeatability of experimental data does not exist over multiple references, as the experiments are difficult to repeat. However, a current focus lies in the reaction between the fluorine atoms in the polymer and the aluminum [7].

Therefore, nanoscale composites like aluminum–fluorine are growing interest due to its attractive properties like the higher density over aluminum– oxygen. Fluorine-rich polymers are especially interesting for their applications as an energetic binder in any type of manufacturing of energetic materials. A lot of work has been done to study the reaction between nanometals as fuel and fluoropolymers as the oxidizer [4,6,7]. Before they were combined with energetics, fluoropolymers have been used for their flame-resistant properties. This is because they are stable and unreactive when fuel is not present. When combined with a fuel though, fluoropolymers have been used for their flammability properties [8]. When aluminum is used as the fuel, the passivating oxide layer of the nAl particles gets destroyed from the oxidizing agents, and the Al-fluoropolymer system ignites. Kappagantula et al. [9] extended on this concept by adding a layer of fluorinated acid to the surface aluminum particles which increased flame velocity.

A pre-ignition reaction (PIR) can be used to describe the exothermic surface reaction that occurs before the main nAl oxidation reaction. Previous research revealed that lower ignition

temperatures and larger exothermic activity emerge from combining nAl with Teflon to create an Al/fluoropolymer mixture [10]. This is caused by the fluorination of the nAl particle shell in process of passivation. This process was manipulated and proven to be sped up with an Al-perfluoro tetradecanoic (PFTD) structure [11]. It was done by lowering the bond dissociation energy from its more sterically hindered structure. Another experiment done at Texas Tech University studied the performance of the thermite-PFPE blends and displayed they are highly dependent on the oxidizing agent [12]. These works show that fluoropolymers such as PFPE can promote reactivity via catalytic behavior of the Al_2O_3 shell which improves the low-temperature surface reactions and aluminum sensitivity.

2.2 Properties of PVDF

Polyvinylidene Fluoride (PVDF) is different from other fluoropolymers in its high piezoelectric properties for a polymer. This material is unique in that it can exist in three phases seen in figure 2.1 described as alpha, beta, and gamma phases. The phases are determined by the arrangement of the molecular structure which can consist of an all trans configuration or a combination of trans and gauche. However, PVDF is only observed to exhibit piezoelectricity in beta and gamma phases due to the orientation of the fluorine and hydrogen atoms [13]. PVDF demonstrates piezoelectric, pyroelectric, and ferroelectric properties at their strongest in the beta phase. Modifications have to be made in order to achieve these desirable properties since PVDF naturally exists in the alpha phase. Luckily, there are feasible methods like stretching or annealing that are well developed to take advantage of these properties. Recent research concludes that doping beta phase PVDF with aluminum nanoparticles increases the piezoelectricity of the material while keeping the important flexibility of the original polymer [4,8]. This infers that PVDF can be an important factor in sensitizing a combustion reaction when in the beta phase.

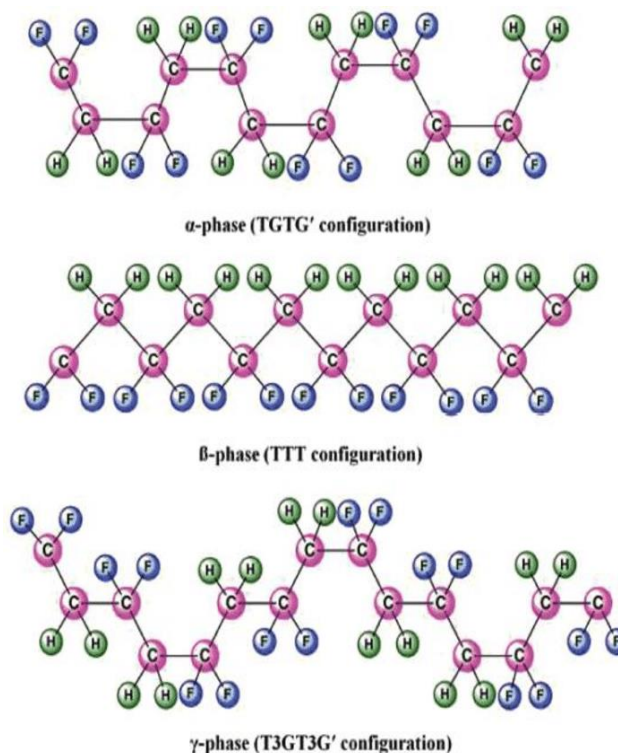


Figure 2.1. The molecular structure of PVDF and its phases [15].

One way to obtain beta phase PVDF without mechanical orientation is to use the co-monomer trifluoroethylene to create PVDF-TrFE [14]. In this phase, the molecules are in an all trans configuration which means all the fluorine molecules are on one side and all the hydrogen molecules are on the other side of the carbon. This leads to the ability the beta phase has in generating the highest spontaneous polarization which shows strong piezoelectric properties. The addition of the co-monomer in PVDF-TrFE introduces more fluorine atoms into the molecular chain causing a steric hindrance effect that prevents alpha phase formation [15]. Huang et al. demonstrated that increasing the mass fraction of beta phase PVDF by ten fold starting at 2.5% in Al-PVDF composites improves peak pressure by 90% and pressure rise rates by 300% [13]. This makes the structure conducive when reacting to form strong Al-F bonds and translates to higher binding energy leading to higher reactivity in the Al/PVDF composite.

Additional annealing or electrical poling treatments can increase the degree of crystallinity and cause alignment of the CF_2 dipoles to produce higher piezoelectric effect. An important parameter to measure in the effectiveness of PVDF is the piezoelectric d_{33} coefficient. The piezoelectric coefficient represents the charge emitted for an applied force. However, the piezoelectric effect is reversible so the opposite is also true. This measurement ensures the

molecules align in order to produce the piezoelectric effect sufficient for sensitization. Poling methods which only work when PVDF is in beta phase which is why this work will look at PVDF-TrFE.

Ferroelectric polymers based on polyvinylidene (PVDF) do not follow the ionic model because they are dipolar order-disorder ferroelectrics. They can be thought of as liquid crystals with a simple mechanical model. This would include wedge-shaped molecules with dipole moment along the wedge axis which exhibits a strong flexoelectric effect [16]. This is similar to PVDF, where the net dipole moment points from the bulky CF_2 side to the CH_2 side of the polymer chain. Baskaran et al. have reported high values for the flexoelectric coefficient up to $82 \mu\text{C}/\text{m}$ in non-ferroelectric PVDF samples. However, PVDF is a polymorphous material so it is hard to rule out the piezoelectric contributions from the residual ferroelectric beta phase. Also, PVDF is a polymorphous material that contains a significant amorphous component and numerous crystalline phases that depend on synthesis and sample preparation [17]. For these reasons, flexoelectricity is hard to measure in one form of PVDF.

2.3 Sensitizing

Piezoenergetic materials are energetics which hold piezoelectric properties. These properties can be exploited for multifunctional purposes. Loose powders tend to have lower times to ignition compared to consolidated media like films, but being able to sensitize films comparable to powders would be advantageous [18]. Polymers such as PVDF, PTFE, PPE, THV, etc. are known to be piezoelectric [3,19-20]. PVDF-TrFE is of particular interest because of its known and well-studied piezoelectric response. PVDF is also a well-known fluoropolymer which makes aluminum a popular choice of addition when forming a reactive material [19]. It has been shown that piezoenergetics can become more sensitized to impact when a DC voltage is applied [7].

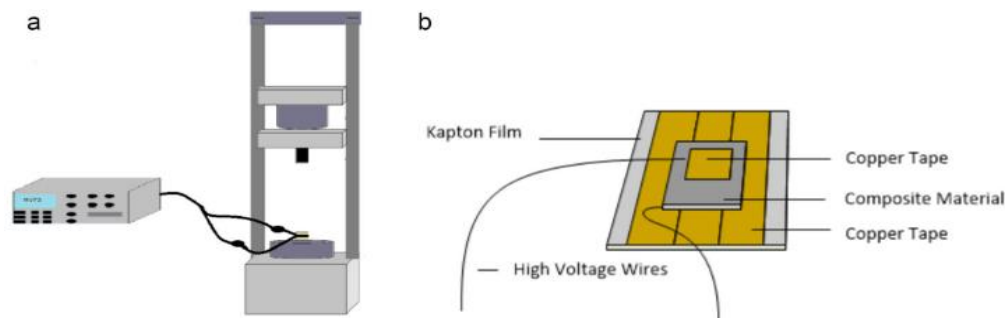


Figure 2.2. The experimental setup for Row and Groven's experiment [7].

Row et al. chose nAl/ fluoropolymer systems to test with a drop weight apparatus (figure 2.2) at a specified height [7]. For the same height, an energetic material would ignite when a voltage was applied but not without one. It was observed that this effect of sensitization would no longer exist after the voltage was turned off for five seconds. This behavior could be explained by a property other than piezoelectricity. Since PVDF is ferroelectric, an external electric field would reverse its spontaneous electric polarization which could affect ignition. Also, the behavior could be described as ‘charge’ since it dissipates with time whereas the effect of poling results in a permanent piezoelectric coefficient.

Fluorine is the main oxidizer in reactions between aluminum and fluoropolymers. The heat of combustion released from a reaction between the fluoropolymer PTFE and aluminum is similar to the heat of combustion of TNT which is one reason for the interest in nanocomposites for EMs. McCollum et al. [21] varied the weight percentages of aluminum added to a PVDF film to study the specific combustion reaction. It was shown that the composite cannot ignite at low concentrations of aluminum since the polymer acts as a heat sink when at lower levels of conductivity. When concentrations of aluminum increase, the heat can travel more easily through the material and a self-propagating burn can occur. Experiments like this show the formulation of Al-fluoropolymer systems can be manipulated through composition and experimental parameters.

These limitations are why the properties of sensitivity and reactivity are being researched on how to control energetics. Recently, there has been increased interest in the development of smart or switchable energetic materials. Materials that can be dialed to a specific yield or can be switched on/off are an example of this. Some efforts to develop smart energetics include electrical solid-state propellants, for applications in aerospace and pyrotechnics [13]. This entails a propellant that is only capable of igniting when a certain voltage is applied. Margevicius from Penn State University applied this concept to piezoenergetics [14]. In her work, nAl/PVDF-TrFE films were given a piezoelectric constant through poling and were shown to increase ignition sensitivity and burn rate when an electric field was applied. This thesis will expand on this concept by utilizing the direct piezoelectric effect through impact sensitivity tests.

2.4 Application to Current Work

This research will focus on the ignition and sensitivity of a nAl/PDF-TrFE composite through manipulation of piezoelectricity introduced by the fluoropolymer. The basis of this work

comes from experiments showing energetic materials can be sensitized with fluoropolymers using the piezoelectric effect by applying a voltage. However, not much research has focused on the characterization of piezoenergetic composite films with varying piezoelectric coefficients. It is difficult to find any other cases of successfully poling these composite materials, especially without the aid of embedded electrodes which would alter the film composition. Therefore, it would be interesting to see a direct comparison of the impact ignition behavior of a poled and unpoled energetic film. Through this background, several concepts were emphasized that are necessary to engage with the desired research. The combination of a fluoropolymer and a nanometal can be considered an oxidizer and a fuel and therefore an energetic material.

3. EXPERIMENTAL METHODS

3.1 Formulation Process

The energetic material used was a nAl/fluoropolymer film fabricated in the laboratory and the process is outlined in figure 3.1. The nAl was purchased from Novacentrix that has 80 nm diameter and used as is. The active nAl content of the powders were 70% as determined by differential scanning calorimetry and thermogravimetric analyzer (DSC/TGA) and shown in a future section. A 70/30 PVDF-TrFE (Polyvinylidene Fluoride and Trifluoroethylene Copolymer) powders were purchased from Arkema and used as is. The final film was composed of 10 % wt. active nAl to ensure that the fabricated film was reactive. The PVDF-TrFE was poured into a solution of dimethylformamide (DMF) at a ratio of 1-gram nAl to 5 mL of DMF. This mixture was then mixed using a high-energy ultrasonic mixer (Branson) at 15% ultrasonic amplitude for 1.5 minutes on, 1.5 minutes off for a total of 3 minutes on. The nAl was then added and the mixture was once again sonicated for 1.5 minutes on, 1.5 minutes off, for a total of 3 minutes on. Once the samples were well mixed, they were cast onto glass slides using a tape caster (MSK-AFA-HC100, MIT) as shown in figure 3.2. The heated bed was set at 125°C and the blade height was 1 mm to achieve near full density films with uniform thickness. The average thickness of the casted film was 85 μm after drying on heated substrate for 15 mins.

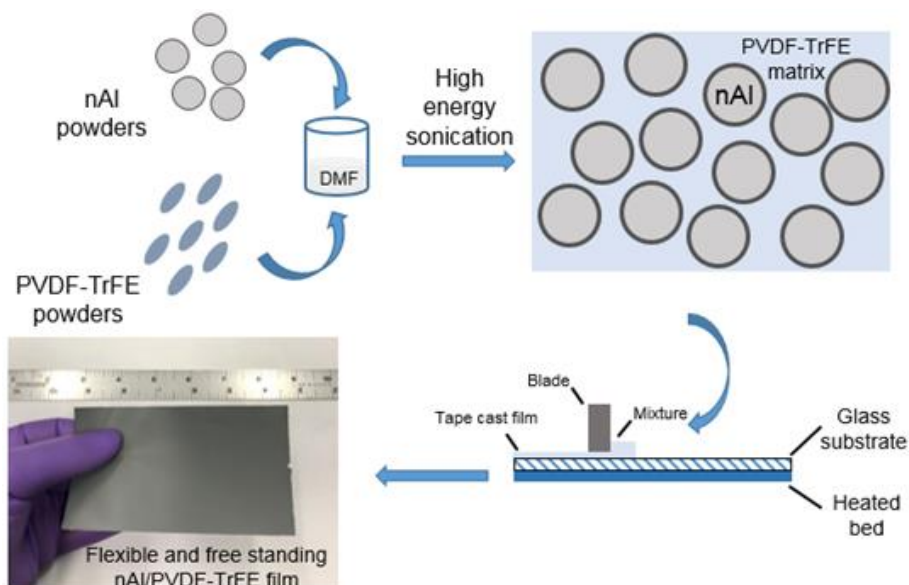


Figure 3.1. Process for film fabrication.

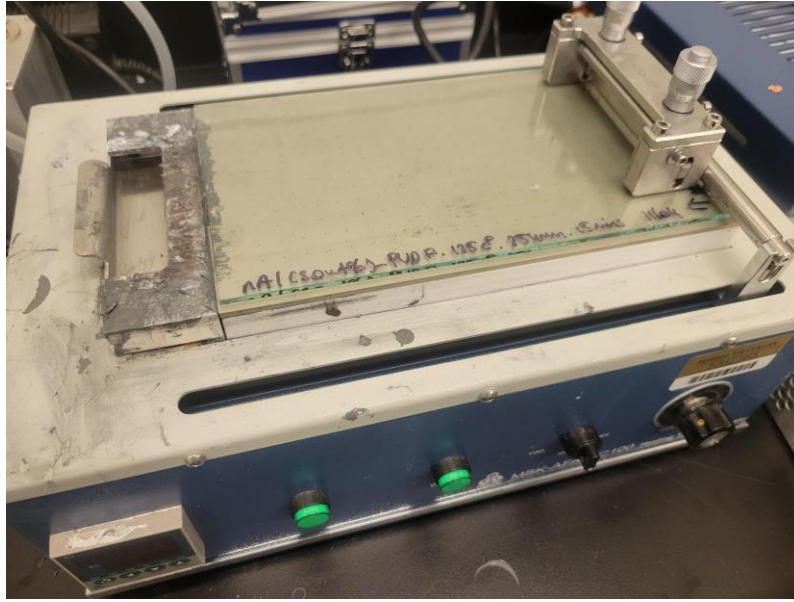


Figure 3.2. Tape caster.

3.2 Poling Process

The two known methods of poling a piezoelectric material with electric field polarization are through direct contact and corona discharge [22]. In both methods, the piezo film is placed between two electrodes. Corona poling is performed with the electrodes separated at a distance so that the voltage potential causes a breakdown in the air and electrons flow through the film in the form of plasma. This method is good for withstanding high electric field values, but the distance away from the sample dampened its effectiveness. The direct method allows for closer contact between the sample and electrodes where the sample can be sandwiched. Margevicius has performed a similar process on nAl/PVDF-TrFE films where she sputtered electrodes onto the film itself [14]. This was not possible for this work because the structure of the films could not be manipulated before impact tests.

After the films were formulated according to the process previously mentioned, a voltage potential was applied to the films using the direct method. Indium tin oxide (ITO) glass slides with conductive surfaces were used as electrodes to sandwich the film and create the electric field. A glass slide with a 1 mm thickness was placed between two ITO glass as a dielectric barrier to prevent electrical breakdown as shown in figures 3.3 and 3.4. The set up was placed on a hot plate set at 75 °C. This is because PVDF-TrFE is more susceptible to poling at elevated temperatures

[23]. It was also important to keep the sample below 90 C because the curie temperature defines the point at which the unstable conformation of the fluorine atoms undergoes transformation, thus losing its piezoelectricity.

The ITO glass slides were connected to a power supply and up to 9 kV were applied through the films before the electrical breakdown occurred. The neat polymer films could withstand even more voltage, but the addition of nAl made the composite films more sensitive to a breakdown. An extensive poling process was conducted to determine the optimal piezoelectric constant (d_{33}) we could achieve with the films. It was determined that 8 kV at 2 minutes yields reproducible results while excessive poling duration does not increase the piezoelectric coefficient which was measured by Berlincourt type piezoelectric tester (PolyK Technologies). Taking into consideration the thickness of the film and dielectric barrier, this is an applied electric field of 7.37 MV/m.

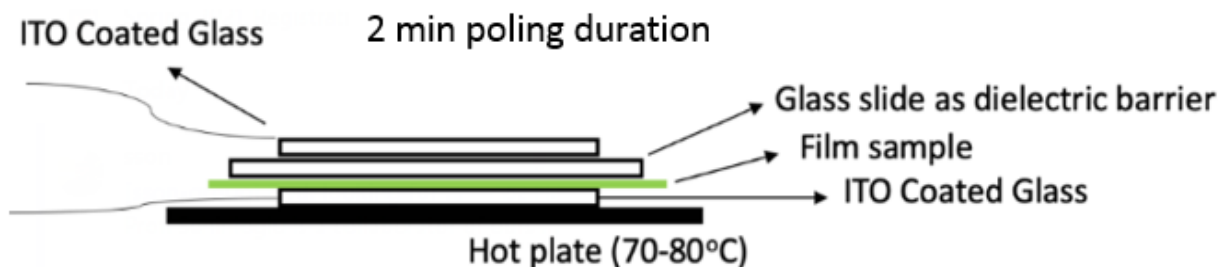


Figure 3.3. Schematic for poling set-up for thin films.

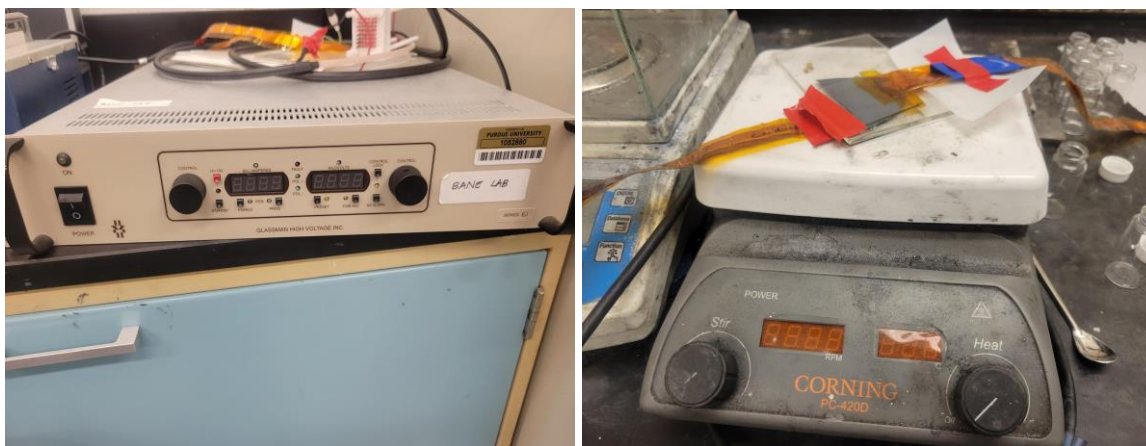


Figure 3.4. High voltage power supply (left) and poling setup (right) used in experiment.

3.3 Characterization of Films

Fourier-transform infrared spectroscopy (FTIR) experiments were performed to determine the possible change in the beta (β) phase in the PVDF-TrFE before and after nAl addition. It was performed at a 2 cm^{-1} spectral resolution by averaging 32 scans using a Perkin Elmer Spectrum 100 spectrometer (Diamond-ATR technique). The beta phase is characterized by the peaks at 844, 1289, and 1425 cm^{-1} [24]. Poling can be achieved for both films, but the magnitude of success may differ.

Field-emission scanning electron microscopy imaging was performed to observe the microstructure of the cross section of the films using a FEI-Nova NanoSEM operated at 5kV. The films were dipped in liquid nitrogen and broken to create a clean-cut edge for imaging. Then, the samples were coated with 20nm thick palladium prior to SEM imaging using Cressington sputter coater.

The most common tool to measure the piezoelectric coefficient of a material is d_{33} meter (figure 3.5) that uses the quasi-static, or Berlincourt, method. Here, the sample is clamped with metal contacts and subjected to a low-frequency force. The electric signals made can be measured and the machine converts it into a d_{33} value with the units of coulombs per newton. This method is quick and effective with the result given within seconds.

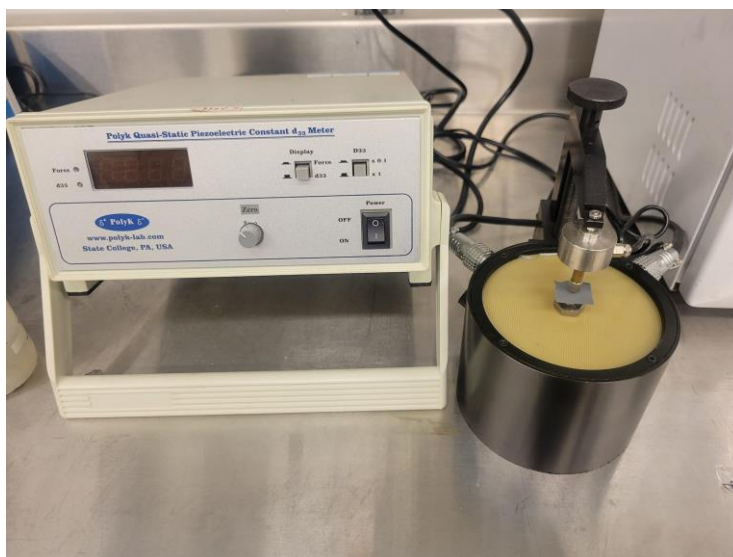


Figure 3.5. Berlincourt type piezometer.

A simultaneous thermal analyzer (Q600 SDT) from TA Instruments was used to determine the weight gain from nAl combustion. This machine takes advantage of a differential scanning

calorimetry (DSC) and thermogravimetric analysis (TGA) to measure both heat flow & weight changes in a material as a function of temperature or time. Figure 3.6 is a graph displaying the reactivity parameters taken from DSC/TGA data for typical nAl powder [25]. There are a few characterization parameters that should be similar to all aluminum powders. The onset temperature where oxidation occurs is around 500 °C. The apparatus will also measure the heat release, degree of oxidation, and oxidation rate at various temperatures. The weight gain can be used to find the active content within the powder.

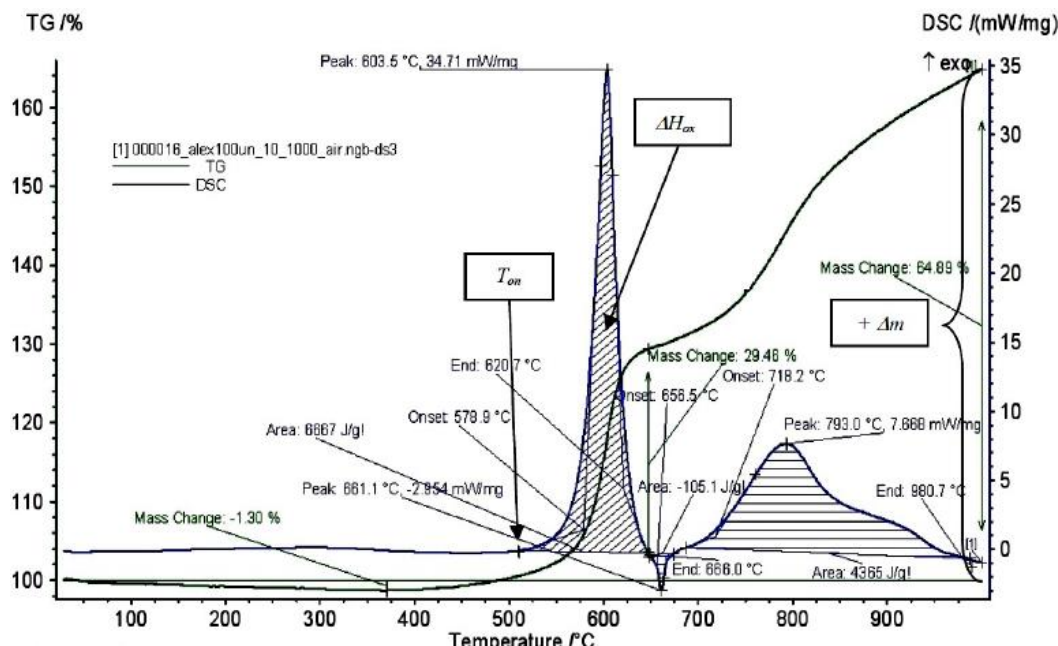


Figure 3.6. Example of DSC/TGA for a typical nanoaluminum powder [25].

3.4 Sensitivity Tests

The current widely utilized statistical test for sensitivity of explosives is the Neyer D-optimal test. This statistical test was designed to efficiently determine the most efficient testing level for sequential sampling based on the go or no-go responses of previous samples. Utilizing the commercial program SenTest™ which allows for rapid determination of the height at which 50% of the samples were expected to ignite, here referred to as the 50% drop height. The distributions and confidence intervals resulting from these tests can then be used to compare the sensitivities of a wide range of energetic materials and compositions. However, due to differences in the design of impact machines, these measures should be generated for each material of interest on the same machine.

The drop weight impact apparatus used is the BAM configuration fall hammer by OZM Research in order to quantify impact sensitivity. This experiment consisted of a weight free falling from a known height and striking an energetic material sample. The tower has heights varying up to a meter and provides guide rails for the 5 kg hammer used in the experiment. The specified BAM configuration was implemented to minimize variability with that starting position. This includes a sample holder consisting of a steel guide ring encapsulating two steel cylinders where the sample is placed in between. The results of the impact were categorized as either go or no go. A go represented a sample that had combusted. A no go represented a sample that had not combusted. This characterization was determined through inspection of the sample post impact along with the presence of an infrared signal from the gain amplified detector. The drop height, as well as initial height for the tests, were determined using the Neyer SenTestTM software for each sample test. The recommended drop height is populated based on the result of the previous test. The software does not provide an indication for when a sufficient number of samples have occurred. Therefore, the approach taken to end the test was to stop after the standard deviation of distribution monotonically decreased over the course of five tests. When the test is complete, the material's 50% probability of explosion drop height and standard deviation values are extracted to analyze the results.

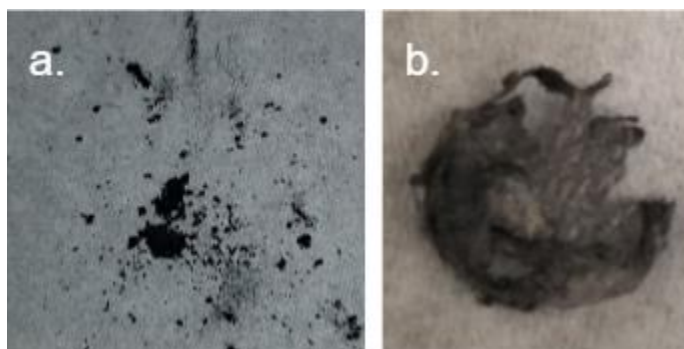


Figure 3.7. Two examples of a sample classified as a go.

Because of the binary nature of the test, a decision had to be made for the samples experiencing incomplete combustion. Any sign of combustion was classified as a go for this test including samples where the entire film was not consumed. Figure 3.7 (a) shows an example of a fully consumed sample as well as a partially consumed sample (b) where part of the film is still intact. Both cases were classified as a go. One reason for this is that there is no difference of the infrared light emitted between an energetic film that was partially consumed versus entirely

consumed from combustion. Also, with safety taken in consideration, any presence of ignition can be dangerous for all types of energetic materials.

3.5 Ignition Delay Tests

The ignition delay was also found using the same drop weight apparatus. However, the procedure consisted of testing samples at five drop heights using 20 cm increments. The time of arrival for the hammer was determined with the response of the piezoelectric films. Wires were attached to the top and bottom metal contacts of where the sample is placed to be able to detect the voltage produced with an oscilloscope. One lead was attached to the bottom pin and the other was in direct connection with the metal hammer. The ignition event was captured using Ge Switchable Gain Amplified Detector from Thorlabs, photodiode in infrared wavelength, paired up with a high-speed camera. A Phantom v2012 was used in conjunction with the experiment to interpret the signals from the oscilloscope at a rate of 100,000 frames per second (fps). The time difference between the first sign of impact and the ignition event was used to determine the ignition delay time. The entire set-up of this experiment is also displayed as a schematic in figure 3.8.

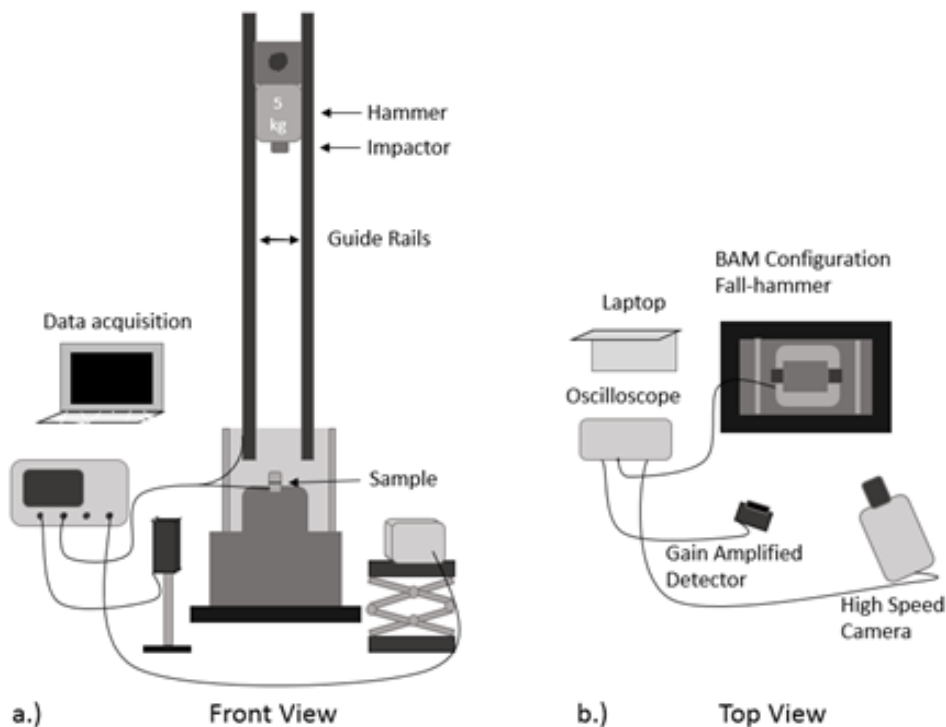


Figure 3.8. Schematic of Experimental Set-up.

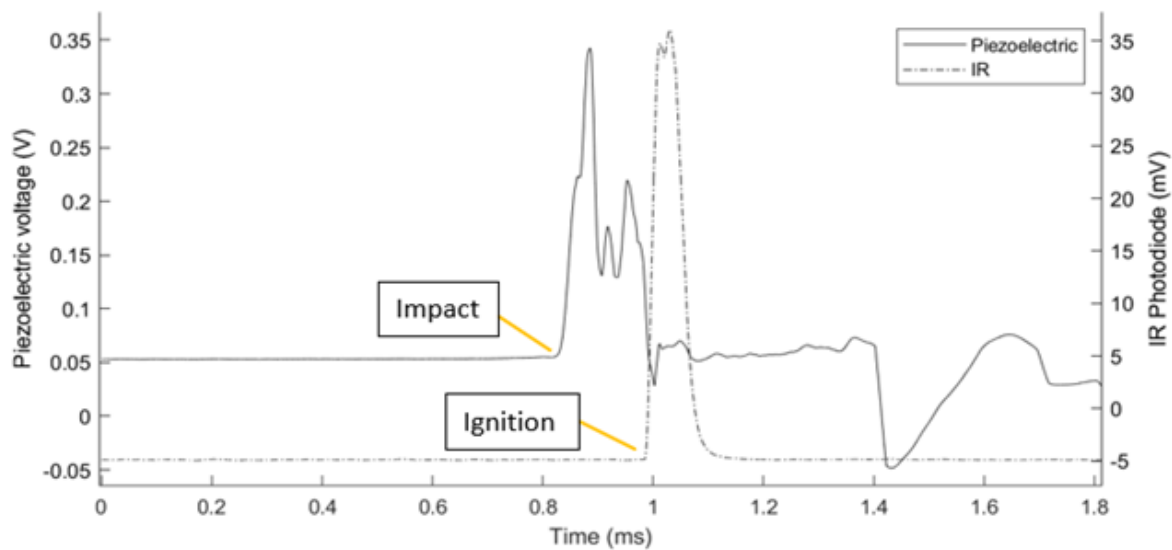


Figure 3.9. Example experimental output for unpoled film at 40 cm.

Figure 3.9 displays an example of the output voltage from the piezoelectric sample along with the signal from the photodiode detecting at the infrared wavelength. The time on the x-axis in figure 3.9 is taken from the oscilloscope which is triggered with the piezoelectric curve and keeps the recordings before the event to ensure nothing is overlooked. The ignition delay is calculated by subtracting the impact start time from the ignition start time which is represented by the first sign of movement from the curves. Also, the magnitude of the piezoelectric voltage was quantified by the oscilloscope, but measurements were not used in this experiment. The piezoelectric properties of the PVDF-TrFE in the energetic composite allowed for a time of arrival measurement to be made with a quick response for both the poled and unpoled films.

4. MODELING

4.1 Microstructure Set-Up

A random microstructure model was generated by a group at Georgia Tech University in a collaborative effort to analyze the ignition sensitivity of a poled and an unpoled nAl/PVDF-TrFE film subjected to a mechanical impact. The microstructure model was created to mimic the samples in the experiment which have a film thickness of 85 μm and comprises aluminum particles that are embedded within the PVDF-TrFE binder. Similar to the experiment, the particle volume fraction is $\eta = 9\%$. This was found by using the determined mass content of nanoaluminum and known densities of the materials. Also, the ratio of the particle's core radius (Al) to the shell thickness (Al_2O_3) is equal to 11.12, and this is consistent with that of the experimental samples, whose core radius and shell thickness are 36.7 nm to 3.3 nm, respectively. Although the particle size was previously verified to be normally distributed based on the small-angle X-ray scattering technique, it is assumed in the present analysis to have a constant diameter for simplicity [26]. Enlarged particles have also been considered as this enables a substantial reduction in the total number of particles required to preserve the volume fraction while also maintaining the same film thickness tested in the experiment, considerably improving the computational efficiency. This difference in the particle size has been observed to have a minor influence on the predicted likelihood of dielectric breakdown during the pre-ignition reaction stage. It is noted that this prediction only accounts for dielectric breakdown and not combustion.

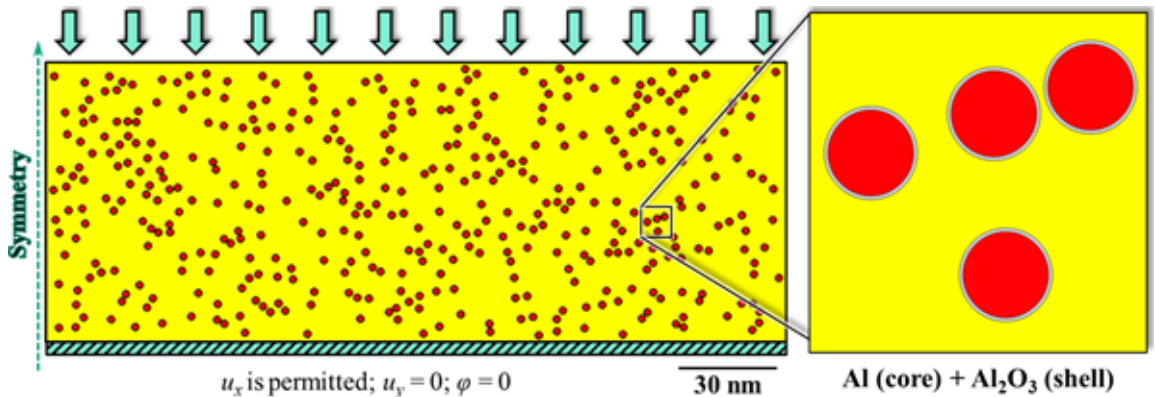


Figure 4.1. A schematic illustration of the mechanical and electrical boundary conditions for the particle/binder composite model. The microstructure has a particle volume fraction of $\eta = 9\%$.

Figure 4.1 shows the microstructure is a two-dimensional model. The simulation analysis is implemented using COMSOL Multiphysics (v5.4). The right surface is charge-free and traction-free. All constituents in the microstructure are initially stress-free and at rest. Further, a symmetry condition is also assumed about the left surface as shown, effectively reducing the geometry to a half-model.

4.2 Governing Equations

The electrostatic response of the material is governed by the conservation of charge (Gauss's Law). The quasi-static mechanical response is governed by the conservation of momentum. The equations are

$$\begin{cases} \text{div}(\mathbf{D}) = \nabla \cdot \mathbf{D} = q_v^\circ \\ \text{div}(\boldsymbol{\sigma}) = \nabla \cdot \boldsymbol{\sigma} = -\mathbf{b}_v \end{cases},$$

where \mathbf{D} and q_v° denote, respectively, the electric displacement vector and free-charge density per unit volume; also, $\boldsymbol{\sigma}$ and \mathbf{b}_v denote the mechanical stress tensor and body-force vector per unit volume, respectively. In the present analysis, $q_v^\circ = 0$ and $\mathbf{b}_v = \mathbf{0}$.

The electric displacement consists of a dielectric polarization term caused by the induced dipole moment, a piezoelectric polarization term caused by the local stress, and a flexoelectric polarization term caused by the local strain gradients. The constitutive relation is

$$D_i = \psi_{ik} E_k + d_{ikl} \sigma_{kl} + \mu_{ijkl} \frac{\partial \varepsilon_{jk}}{\partial x_l},$$

where E_k and $\partial \varepsilon_{jk} / \partial x_l$ denote the electric field and strain gradient, respectively; ψ_{ik} , d_{ikl} , and μ_{ijkl} represent the absolute permittivity, piezoelectric coefficient, and flexoelectric coefficient tensors, respectively. An isotropic permittivity is assumed for all constituents of the microstructure. The

electric field vector can be further expressed as $E_k = -\partial\varphi/\partial x_k$, where φ denotes the scalar electric potential field in the material.

The Green-Lagrangian finite strain tensor can be related to the displacement via

$$\boldsymbol{\varepsilon} = \frac{1}{2}(\mathbf{F}^T \mathbf{F} - \hat{\mathbf{I}}) = \frac{1}{2}[(\nabla \mathbf{u}) + (\nabla \mathbf{u})^T + (\nabla \mathbf{u})^T (\nabla \mathbf{u})],$$

where \mathbf{F} and $\hat{\mathbf{I}}$ represent the deformation gradient tensor and the identity tensor, respectively; and $\mathbf{u} = \mathbf{u}(\mathbf{x})$ indicates the displacement vector at a material point, \mathbf{x} .

As the deformation is assumed to be quasi-static, the rate-dependence of the constitutive behaviors is not considered. The coupled electromechanical stress tensor can be written as

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} - d_{kmn} C_{mnij} E_k + \mu_{lijk} \frac{\partial E_l}{\partial x_k},$$

where C_{ijkl} represents the elastic stiffness tensor.

4.3 Modeling Prediction

To analyze the ignition sensitivity of the nAl/PVDF-TrFE composite film under a dynamic impact, the induced electrical responses are first examined. Figure 4.2 shows the electric potential and electric field distributions for both poled and unpoled films under the external impact load with a drop height of 20 cm. While the level of voltage generation (φ) is trivial within unpoled films, poled films generate an appreciable voltage upon a mechanical impact, owing to the binder's piezoelectric properties.

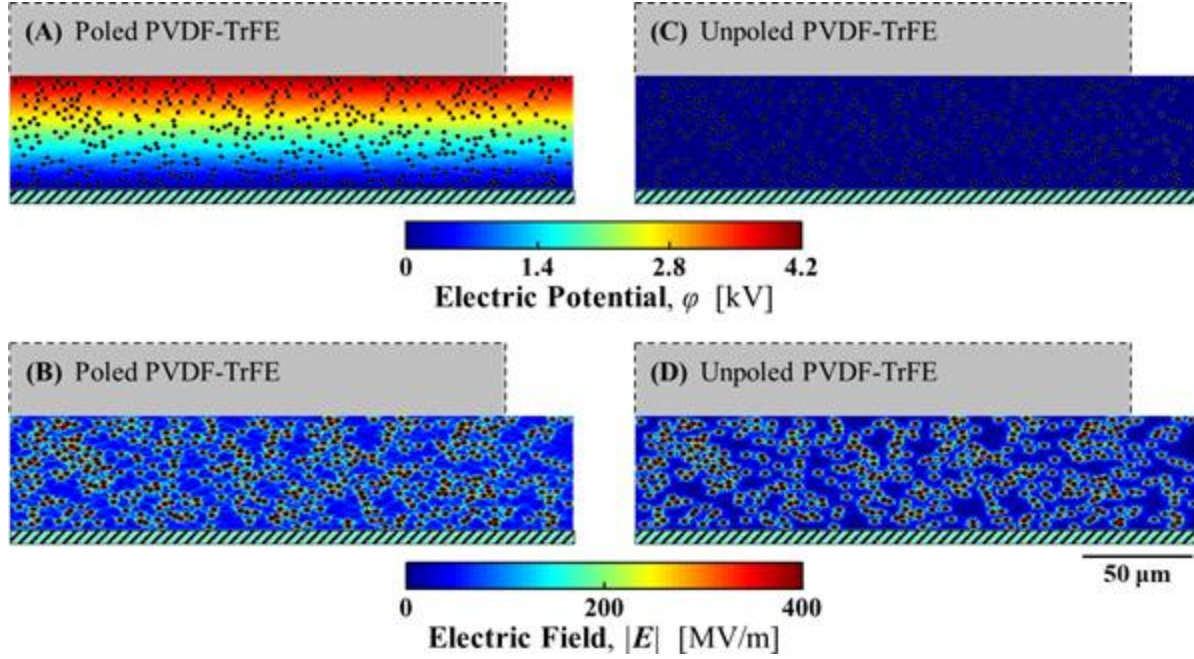


Figure 4.2 The distributions of induced electric potential and electric field within (a-b) a poled and (c-d) an unpoled film for the microstructure. The deformation corresponds to a drop-height of $h_0 = 20$ cm at $t = 109 \mu\text{s}$.

Several electromechanical responses, including the underlying polarization and the resulting electric field, are also delineated in Fig. 4.2 for a poled film at $109 \mu\text{s}$ under a drop height of 20 cm. The stress and strain gradient near the binder/particle interfaces induce piezoelectric and flexoelectric polarization, respectively. While the piezoelectric polarization simply depends on whether the film is poled or not, significant flexoelectric polarization is developed near the particle interfaces in both poled and unpoled films, owing to their high strain gradients. For poled films as an example, the binder experiences a high interfacial enhancement (i.e., the ratio of the local interfacial response to the average bulk response in the binder) of electric displacement (~ 6.9) and electric field (~ 5.2).

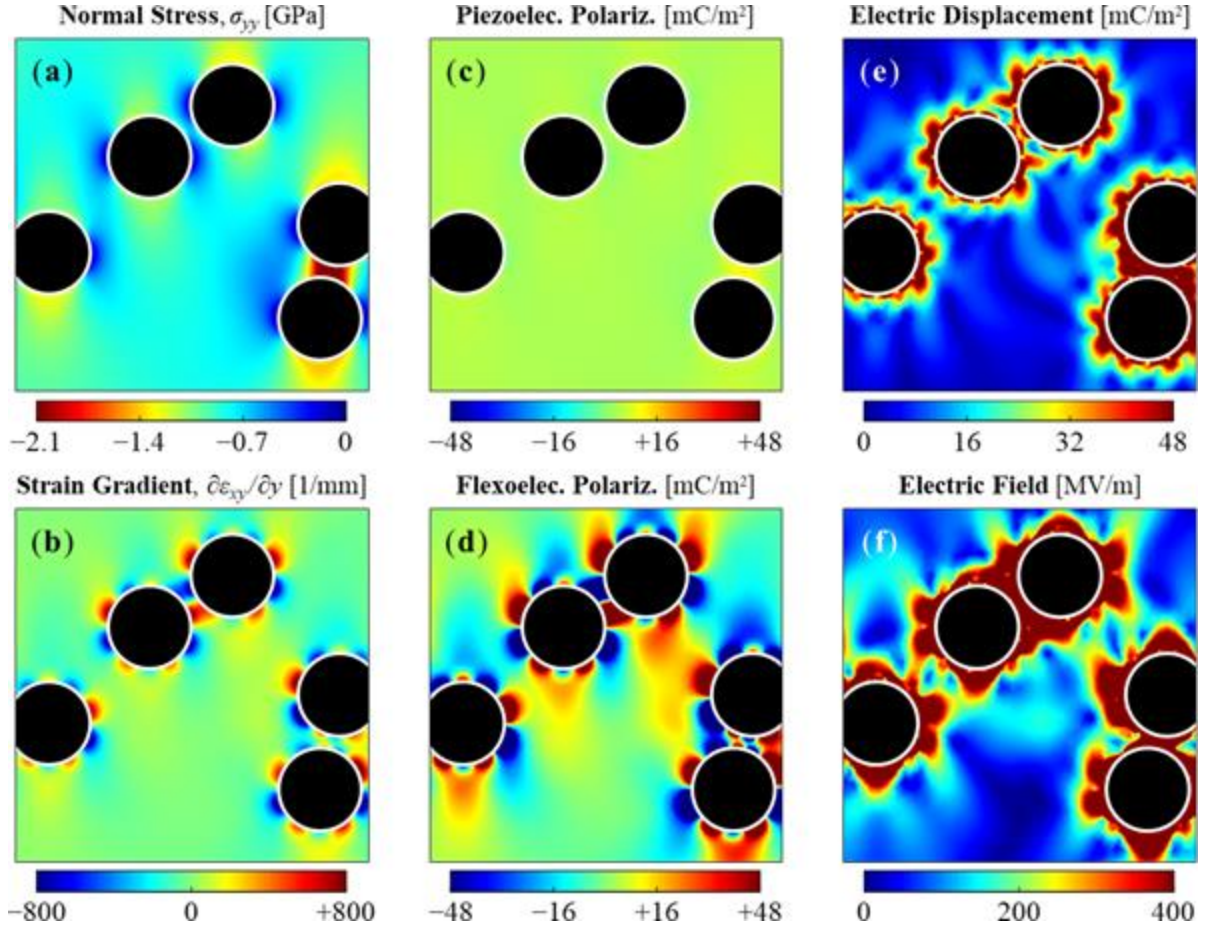


Figure 4.3. An inset view of the electromechanical responses in the poled film near the particles at $t = 109 \mu\text{s}$ for $h_0 = 20 \text{ cm}$. (a) normal stress along the y-direction (b) shear strain gradient (c) piezoelectric polarization along the y-direction (d) flexoelectric polarization along the y-direction (e) electric displacement magnitude (f) electric field magnitude.

Further, figure 4.3 illustrates the temporal evolution of the E-field for a poled film under a drop height of 20 cm. Here, it can be seen that the interfacial E-field near the particles rises over time and eventually reaches the breakdown strength of the PVDF-TrFE binder ($E_{bd} = 400 \text{ MV/m}$). The E-field of an unpoled film is determined by the flexoelectric polarization since no response was given from the piezoelectric polarization.

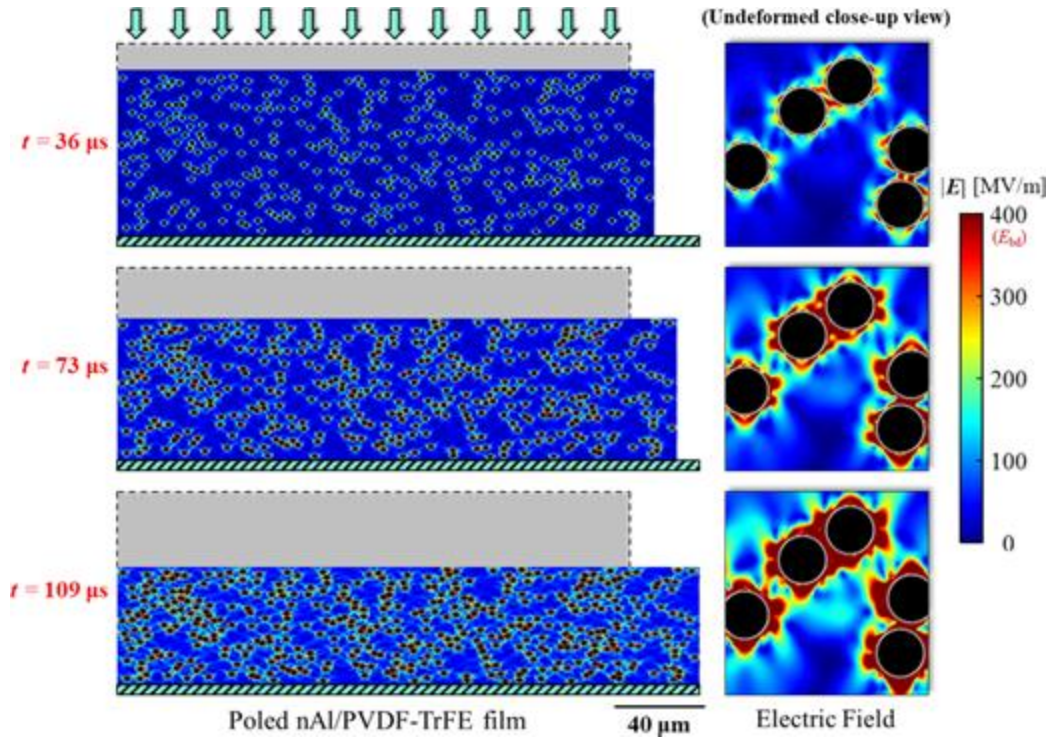


Figure 4.4. Evolution of the electric field magnitude ($|E|$) within the poled binder for $h_0 = 20$ cm.

The ignition sensitivity of the film is characterized by predicting the likelihood of dielectric breakdown along the binder/particle interfaces. It is noted that several nonlinear processes have not been explicitly considered as their influence is assumed to be inconsequential as follows. First, the heat dissipated by the electrical discharge during the breakdown is not modeled as the ignition threshold has been defined as the earliest time at which point the critical interfaces reach the breakdown strength, obviating the need for capturing the complex post-breakdown processes. Moreover, the heat dissipated by the chemical reactions within the film is also not modeled, due to the fact that the primary scope of this threshold analysis is limited to the PIR stage. As the breakdown process is not explicitly modeled, the likelihood of an interfacial breakdown is therefore quantified as the extent to which the interfacial E-field is in exceedance of the binder's breakdown strength.

In addition, other auxiliary mechanisms contributing to the thermal runaway and ultimately the ignition of the energetic films have been explicitly considered but in a separate nonlinear, dynamic, thermomechanical analysis. These mechanisms solely comprise the heat dissipations caused by the viscoelasticity of the PVDF-TrFE binder and the viscoplasticity of the aluminum particles. The binder's viscoelasticity is modeled using the Standard Linear Solid model (SLS).

The elastic-viscoplastic response of the particles is modeled using the Perzyna model and the Ludwik model for isotropic hardening. The highest temperature rise caused by the two mechanical dissipations is limited to only ~ 1 K in the aluminum particles under a drop height of 100 cm, indicating that the heat generated by mechanical dissipations is negligible for a drop height ranging between 20 cm and 100 cm.

5. FILM CHARACTERIZATION

5.1 SEM Imaging

SEM micrographs taken from the cross-sections of the nAl/PVDF-TrFE films show that nAl particles were successfully dispersed in the PVDF matrix. A representative image of the 10 wt.% nAl/PVDF-TrFE film dried at 125°C is shown in figure 5.1. A lower magnification image in figure 5.1 (a and c) shows the solid film with little to no porosity on a macroscopic scale. A higher magnification nanoscale image figure 5.1 (f) shows that the individual 80 nm aluminum particles dispersed in the PVDF matrix while still maintaining little porosity. In the nanoscale image, branches of the PVDF binder can be seen throughout the sample, which can be attributed to the sample preparation for imaging, where the samples were shattered in liquid nitrogen.

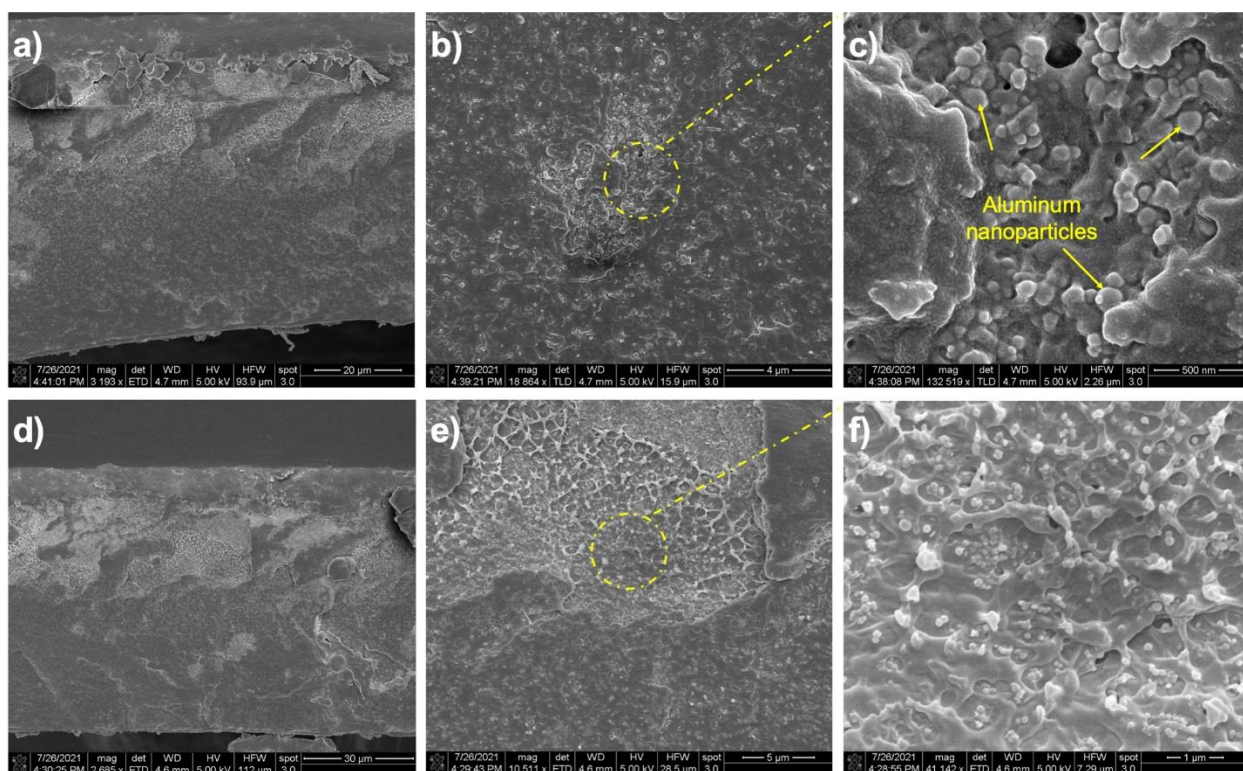


Figure 5.1. SEM images of nAl/PVDF-TrFE with a side view (a)(d) and a zoomed in view (b)(e). Close-ups show a case with nAl agglomerated (c) and nAl particles dispersed within the fibrous PVDF-TrFE (f).

The porosity of the films is controlled by the temperature of the tapecaster bed during casting. By increasing 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 nAl/PVDF-TrFE to form films with higher

density. Image (c) in figure 5.1 shows a close-up of nAl particles that agglomerated together due to improper mixing. It can also be observed that the nAl particles vary in size under 100 nanometers. Image (f) displays what the particles should look like when dispersed properly within the fibrous PVDF-TrFE. A drying temperature of 125 °C was found to consistently have no macroscopic porosity and is used as the full density sample for solids loading experiments. This was also confirmed with an Archimedes density tester using the buoyancy technique. The results show that the composite film had a theoretical max density of 97%.

5.2 FTIR Analysis

Fourier-transform infrared spectroscopy (FTIR) experiments were run to determine the existence of beta phase in the PVDF-TrFE before and after the addition of nAl. The beta phase is indicated by the peak at 1289 cm⁻¹ for both the neat PVDF-TrFE and nAl/PVDF-TrFE composite films. The neat film shows that the beta phase is readily present in the tape casted film as marked with the arrows on figure 5.2. After the addition of nAl, it was observed that the intensities of peaks pertaining to the beta phase and their relative intensities increases, which may indicate the increased β phase formation within the tape casted films. This may be due to the increased nucleation regions caused by the addition of nAl that would facilitate β phase formation. It should also be mentioned that the tape casted neat PVDF-TrFE film is translucent while the nAl added film is dark in color and opaque. This manifest itself with the dramatic decrease in overall transmittance in the spectrum after nAl addition. Overall, the FTIR results indicate that nAl/PVDF-TrFE film can be poled.

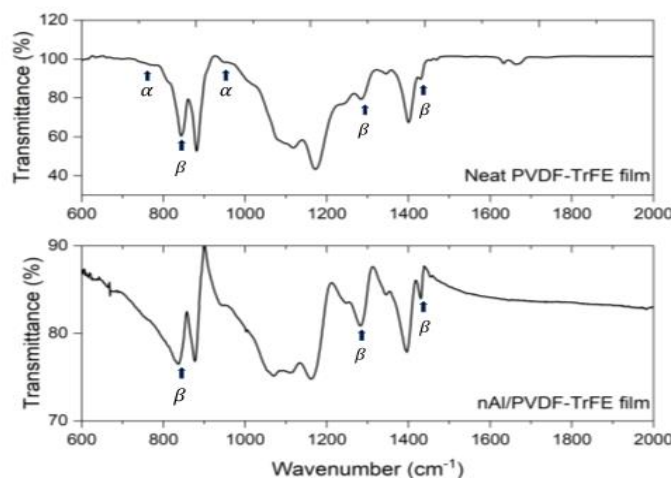


Figure 5.2. FTIR of neat PVDF-TrFE and 10wt% Al in composite film.

5.3 Piezoelectric Coefficient Measurement

The electric field poling was conducted for nAl/PVDF-TrFE films at the operating voltage of 8 kV for 5 mins. The effective applied electric field was calculated by dividing applied voltage to the total thickness of dielectric barrier and sample thickness, which results in applied electrical field of 73 kV/cm. The poled nAl/PVDF-TrFE films being tested had a d_{33} value average of 5.45 pC/N with a standard deviation of 0.38 pC/N determined by Berlincourt type piezoelectric tester and the unpoled samples were confirmed to have no piezoelectric response.

5.4 DSC/TGA Analysis

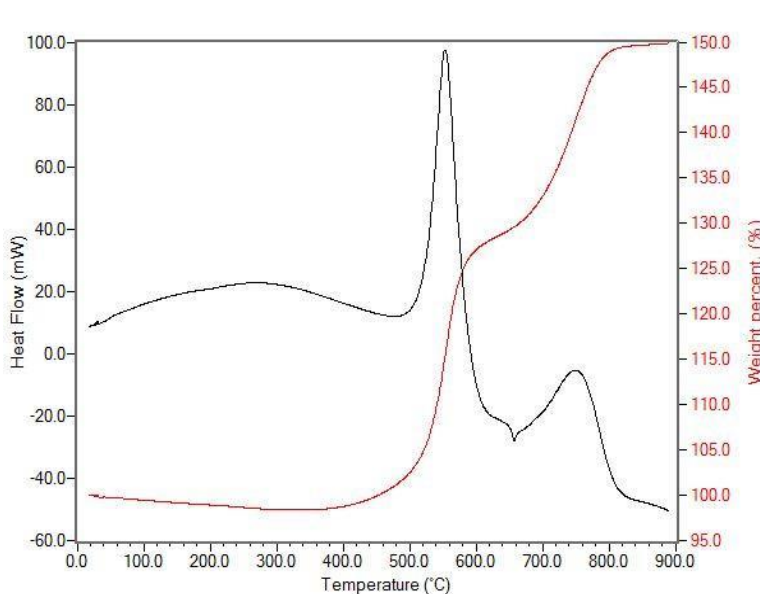


Figure 5.3. DSC/TGA of nAl.

The thermal analysis (figure 5.3) shows that the onset temperature does occur around 500 °C as expected. As the nanoaluminum is oxidized the mass increases to about 157% of its original weight. The molecular weight of Al and Al_2O_3 is 27 and 102 g/mol 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 values, we are able to conclude the nanoaluminum used was 67% active.

6. IMPACT TESTS

6.1 Sensitivity Test

The experimental results for the films were captured and displayed in Figure 6.1 as cumulative probability plots based on the estimated drop height, standard deviation, and an assumed normal distribution. Figure 6.1 shows that the poled film was more sensitive to impact than the film with no piezoelectric coefficient. The height for a 50% probability of ignition for the poled samples was 10.41 cm whereas the height for unpoled was 11.3 cm. The 0.91 cm difference can be attributed to the sensitization of the poled films from the piezoelectric effect. To satisfy the Neyer SenTest™, a total of 45 and 51 samples were tested for unpoled and poled films, respectively.

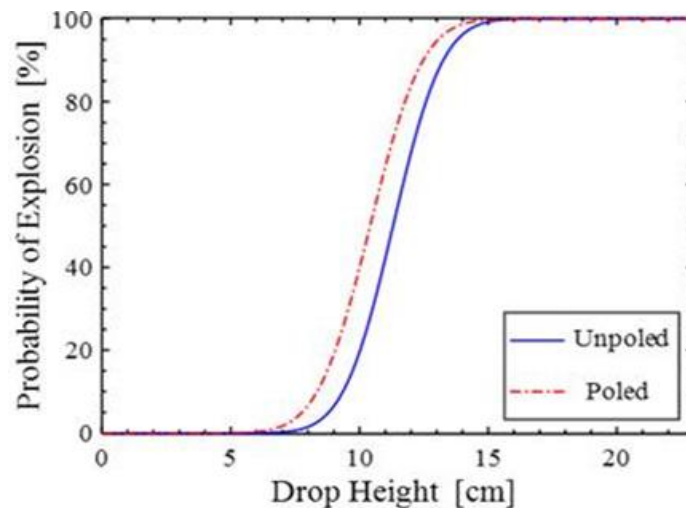


Figure 6.1. Cumulative Distribution Function of sensitivity of films.

6.2 Ignition Delay Test

The initiation of impact is defined as the moment when the hammer contacts the top steel cylinder and compression of the sample begins. This event coincides with time of arrival signaled by the voltage produced by the sample itself. Figure 6.2 shows a time lapse of the subsequent ignition event for an unpoled film with a drop height of 40 centimeters. The flash, if present, is indicated for each timeframe by a yellow arrow. For this trial, ignition occurs at about 150 microseconds and can be observed as a faint flash in the video. The ignition event has a duration

of about 170 microseconds. A similar event takes place for the poled PVDF-TrFE/nAl film but the ignition occurs earlier.

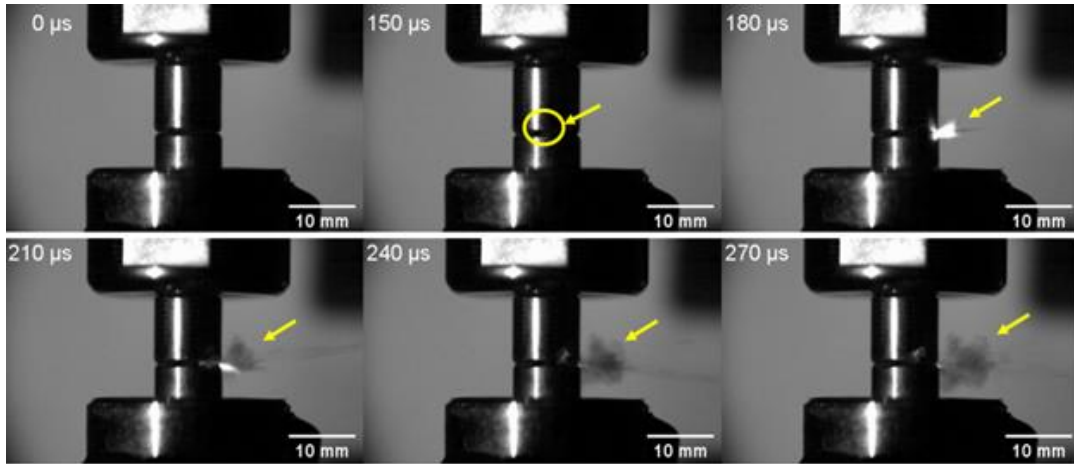


Figure 6.2. Ignition event caught by Phantom v2012 camera.

The thresholds have been similarly determined for a range of drop heights between 20 cm and 100 cm and have been compared to the experimental results. As indicated by the exponential regression curves of the times-to-PIR shown in Fig. 6.3, the predicted thresholds for both poled and unpoled films vary with a monotonically decreasing trend as the impact load is increased. Poled films also generally have quicker times-to-PIR than unpoled films, demonstrating the ability to tailor their ignition sensitivities via piezoelectricity. In the specific case of nAl/PVDF-TrFE films, however, poling is shown to render only a tenuous effect on the sensitivity, as the predicted threshold for poled films only differs from that of unpoled films by $\sim 2.6\%$. The reason for this weak effect is that the electromechanical polarizations predominantly stem from the strong flexoelectric properties of the binder.

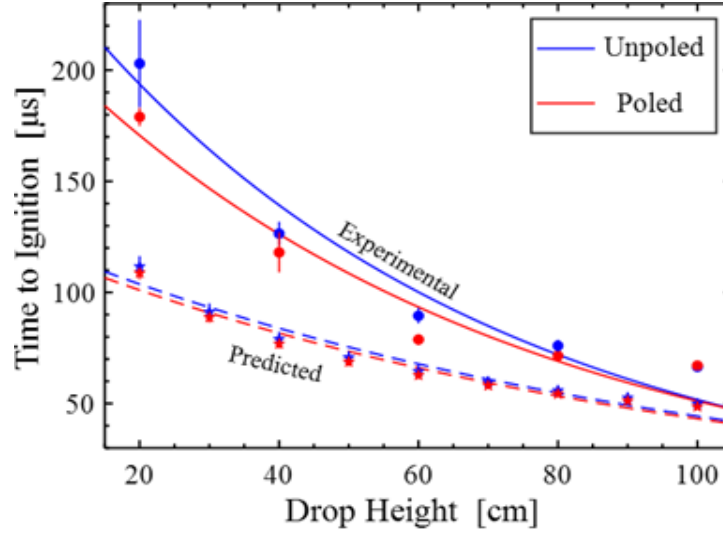


Figure 6.3. Comparison of thresholds showing the predicted time-to-PIR (dashed lines) and the experimental time-to-ignition (solid lines) for poled and unpoled films.

For ignition delay, there is a negative correlation between height and delay time for both samples as expected. A total of 25 samples were tested for each drop height. The differences between the poled and unpoled samples are more apparent with lower drop heights and diminish as heights increase. At 20 cm, the average delay time for a poled and unpoled sample is 179 μs and 203 μs , respectively. This suggests that the piezoelectric effect catalyzes the ignition process. This effect plays less of a role at higher impact energies since there is almost no difference between the two samples at a height of 100 cm.

7. SUMMARY AND CONCLUSIONS

7.1 Conclusion

In this study, we have fabricated and poled PVDF-TrFE/nAl composite films to create piezoelectric energetic material. The piezoelectric polymer was confirmed to retain the beta phase content with the addition of nanoaluminum. Furthermore, the piezoenergetic film was given a piezoelectric constant value of 5.45 pC/N through conventional poling methods. Then, the drop weight impact sensitivity of the films with a piezoelectric response and the unpoled films which do not exhibit piezoelectric response were investigated using a BAM configuration drop-weight test setup and the results were analyzed by Neyer Sensitivity tests. The test concluded that the poled nAl/PVDF-TrFE films required less energy to ignite than the unpoled films. We have also shown that the piezoelectric films show a somewhat decrease in ignition delay time as compared to unpoled films, which suggests that piezoelectricity catalyzes the ignition process. Finally, we successfully demonstrated the use of a piezoelectric reactive as a time of arrival gauge by measuring the output dynamically.

Although piezoelectricity was the only cause of the change in sensitivity, flexoelectricity showed to play a huge role in the computer models. The electric field was dominated by the flexoelectric polarization and went unchanged from unpoled to poled. This alone caused the samples to reach the dielectric breakdown of the PVDF-TrFE binder. The model also showed that the addition of the piezoelectric constant decreased the ignition delay time by a miniscule amount. The magnitude of the piezoelectric effect was measured, but more research needs to be conducted to quantify the effect of flexoelectricity on ignition behavior. These results could pave the way for using inherent properties from polymers to control the sensitivity of smart energetics. Further efforts should focus on other forms of ignition, an increase in piezoelectric coefficient for piezoenergetics, and additional fluoropolymer/metal systems.

7.2 Future Work

This research explored the sensitivity of energetics with piezoelectricity during impact. Further work needs to be done for other characterization methods like friction or thermal sensitivity. Also, other materials should be included in future experiments to better understand the

piezoelectric behavior. This could be done with aluminum and other piezoelectric polymers or even cellulose. This work could also be implemented with explosives such as PETN which has known piezoelectric properties. The demonstration of the reactive gauge used in this research can also be incorporated with explosives to characterize properties like the rate of detonation.

In addition to the different materials that should be tested, different processes to formulate these films should be analyzed as well. This could contribute to films with desirable properties to pole like max density and uniform thickness. Another reason to explore more methods of fabrication could be to contribute to the commercial viability and lead to a larger scale of production.

REFERENCES

- [1] Meda, L., G. Marra, Luciano Galfetti, Febo Severini, and Luigi De Luca. "Nano-aluminum as energetic material for rocket propellants." *Materials Science and Engineering: C* 27, no. 5-8 (2007): 1393-1396.
- [2] Sambamurthi, Jayaraman K., Edward W. Price, and Robert K. Sigman. "Aluminum agglomeration in solid-propellant combustion." *AIAA journal* 22, no. 8 (1984): 1132-1138.
- [3] Jackson, T. L., F. Najjar, and J. Buckmaster. "New aluminum agglomeration models and their use in solid-propellant-rocket simulations." *Journal of Propulsion and Power* 21, no. 5 (2005): 925-936.
- [4] Valluri, Siva Kumar, Mirko Schoenitz, and Edward Dreizin. "Fluorine-containing oxidizers for metal fuels in energetic formulations." *Defence Technology* 15, no. 1 (2019): 1-22.
- [5] Sundaram, Dilip Srinivas, Vigor Yang, Ying Huang, Grant A. Risha, and Richard A. Yetter. "Effects of particle size and pressure on combustion of nano-aluminum particles and liquid water." *Combustion and Flame* 160, no. 10 (2013): 2251-2259.
- [6] Janesheski, Robert S., Lori J. Groven, and Steven Son. "Fluoropolymer and aluminum piezoelectric reactives." In *AIP Conference Proceedings*, vol. 1426, no. 1, pp. 741-744. American Institute of Physics, 2012.
- [7] Row, Sara L., and Lori J. Groven. "Smart Energetics: Sensitization of the Aluminum-Fluoropolymer Reactive System." *Advanced Engineering Materials* 20, no. 2 (2018): 1700409.
- [8] Mulamba, Oliver, and Michelle Pantoya. "Combustion Characterization of Energetic Fluoropolymer Composites." *Handbook of Fluoropolymer Science and Technology* (2014): 363-376.
- [9] Kappagantula, Keerti, Michelle L. Pantoya, and Emily M. Hunt. "Impact ignition of aluminum-teflon based energetic materials impregnated with nano-structured carbon additives." *Journal of Applied Physics* 112, no. 2 (2012): 024902.
- [10] Osborne, Dustin T., and Michelle L. Pantoya. "Effect of Al particle size on the thermal degradation of Al/Teflon mixtures." *Combustion Science and Technology* 179, no. 8 (2007): 1467-1480.

- [11] Kappagantula, Keerti S., Cory Farley, Michelle L. Pantoya, and Jillian Horn. "Tuning energetic material reactivity using surface functionalization of aluminum fuels." *The Journal of Physical Chemistry C* 116, no. 46 (2012): 24469-24475.
- [12] McCollum, Jena, Michelle L. Pantoya, and Scott T. Iacono. "Activating aluminum reactivity with fluoropolymer coatings for improved energetic composite combustion." *ACS applied materials & interfaces* 7, no. 33 (2015): 18742-18749.
- [13] Huang, Sidi, Sungwook Hong, Yingchun Su, Yue Jiang, Shogo Fukushima, Thomas Mark Gill, Nil Ezgi Dincer Yilmaz et al. "Enhancing combustion performance of nano-Al/PVDF composites with β -PVDF." *Combustion and Flame* 219 (2020): 467-477.
- [14] Margevicius, Madeline Alma. "SENSITIZING ENERGETIC MATERIALS USING PIEZOELECTRICITY." (2019)
- [15] Li, Yuchao, Chengzhu Liao, and Sie Chin Tjong. "Electrospun polyvinylidene fluoride-based fibrous scaffolds with piezoelectric characteristics for bone and neural tissue engineering." *Nanomaterials* 9, no. 7 (2019): 952.
- [16] Meyer, Robert B. "Piezoelectric effects in liquid crystals." *Physical Review Letters* 22, no. 18 (1969): 918.
- [17] Davis, G. T., J. E. McKinney, M. G. Broadhurst, and SCi Roth. "Electric-field-induced phase changes in poly (vinylidene fluoride)." *Journal of Applied Physics* 49, no. 10 (1978): 4998-5002.
- [18] Moore, Kevin, Michelle L. Pantoya, and Steven F. Son. "Combustion behaviors resulting from bimodal aluminum size distributions in thermites." *Journal of Propulsion and Power* 23, no. 1 (2007): 181-185.
- [19] Harrison, J. S., and Zoubeida Ounaies. *Piezoelectric polymers*. NASA Langley Research Center. Institute for Computer Applications in Science and Engineering [ICASE], 2001.
- [20] Gerhard-Multhaupt, R., W. Kunstler, T. Gome, A. Pucher, T. Weinhold, M. Seiß, Zhongfu Xia, A. Wedel, and R. Danz. "Porous PTFE space-charge electrets for piezoelectric applications." *IEEE Transactions on Dielectrics and Electrical Insulation* 7, no. 4 (2000): 480-488.
- [21] McCollum, Jena, Aimee M. Morey, and Scott T. Iacono. "Morphological and combustion study of interface effects in aluminum-poly (vinylidene fluoride) composites." *Materials & Design* 134 (2017): 64-70.

- [22] Cholleti, Eshwar Reddy. "A Review on 3D printing of piezoelectric materials." In *IOP Conference Series: Materials Science and Engineering*, vol. 455, no. 1, p. 012046. IOP Publishing, 2018.
- [23] Chan, H. L. W., M. C. Cheung, and C. L. Choy. "Study on BaTiO₃/P (VDF-TrFE) 0–3 composites." *Ferroelectrics* 224, no. 1 (1999): 113-120.
- [24] Chen, Shuting, Kui Yao, Francis Eng Hock Tay, and Lydia Li Shan Chew. "Comparative investigation of the structure and properties of ferroelectric poly (vinylidene fluoride) and poly (vinylidene fluoride–trifluoroethylene) thin films crystallized on substrates." *Journal of applied polymer science* 116, no. 6 (2010): 3331-3337.
- [25] Gromov, Alexander, Luigi T. DeLuca, A. P. Il'In, Ulrich Teipel, A. Petrova, and D. Prokopiev. "Nanometals in energetic systems: achievements and future." *International Journal of Energetic Materials and Chemical Propulsion* 13, no. 5 (2014).
- [26] Bottero, J. Y., D. Tchoubar, J. M. Cases, and F. Fiessinger. "Investigation of the hydrolysis of aqueous solutions of aluminum chloride. 2. Nature and structure by small-angle X-ray scattering." *The Journal of Physical Chemistry* 86, no. 18 (1982): 3667-3673.