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14. ABSTRACT

The effort to realize advanced munitions using high-performance, safe energetic materials has generated interest in nano-composite energetic materials. A particular class composites, nano-aluminum (nAl)/fluoropolymer composites, are of interest due to their high densities and performance-enhancing capabilities. In particular, these composites have been demonstrated ignition sensitization by means of charge application, potentially due to the piezoelectric properties of the fluoropolymer. In the current work, potential nAl/fluoropolymer systems were

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Report Title

Final Report: Research Area 11.1 STIR: Investigation of Piezoelectric Reactives as Tunable Energetics for Advanced Munitions

ABSTRACT

The effort to realize advanced munitions using high-performance, safe energetic materials has generated interest in nano-composite energetic materials. A particular class composites, nano-aluminum (nAl)/fluoropolymer composites, are of interest due to their high densities and performance-enhancing capabilities. In particular, these composites have been demonstrated ignition sensitization by means of charge application, potentially due to the piezoelectric properties of the fluoropolymer. In the current work, potential nAl/fluoropolymer systems were studied to improve understanding of their ignition, combustion, and piezoelectric characteristics. Methods were developed for synthesizing nAl/fluoropolymer composite films for the consistent and controlled production of test samples. Experiments were then conducted to investigate the sensitization of these composites by charge application, electrical poling, and inert doping. Piezoelectric behavior of the composites resulting from doping and electrical poling was demonstrated. Drop weight ignition experiments showed that the ignition sensitivity of electrically poled samples could be controlled using an electric field. In addition, the burn rate of nAl/fluoropolymer sheets was significantly enhanced under the influence of an electric field. Finally, nAl/THV composites were shown to be susceptible to photoflash ignition. These results demonstrate the potential for using these composites as tailored energetic materials and as additives for sensitivity control in other energetic systems.

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Steven Son	0.07	
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Final Report: Research Area 11.1

STIR: Investigation of Piezoelectric Reactives as Tunable Energetics for Advanced Munitions

Omar R. Yehia[1], Brian M. Howell[2], Prof. Ibrahim E. Gunduz[1], Prof. Steven F. Son[1], Prof. Sally P. Bane[3]

[1]School of Mechanical Engineering, Purdue University, West Lafayette, IN 47906
[2]School of Chemical Engineering, Brigham Young University, Provo, UT 84602
[3]School of Aeronautics and Astronautics Engineering, Purdue University, West Lafayette, IN 47906

EXECUTIVE SUMMARY

The effort to realize advanced munitions through the use of high-performance and safe energetic materials has led to the interest in nano-composite energetic materials. A particular class of energetic materials, nano-aluminum/fluoropolymer composites, are of interest due to their high densities and performance-enhancing capabilities in explosive, propellant, and pyrotechnic applications. In particular, the nano-aluminum (nAl)/fluoropolymer system has been demonstrated to exhibit susceptibility to ignition sensitization by means of charge application, potentially due to the piezoelectric properties of the fluoropolymer. In the current work, potential nAl/fluoropolymer systems were studied to improve our understanding of their ignition, combustion, and piezoelectric characteristics. First, synthesis procedures were developed for preparing nAl/fluoropolymer composite films for the consistent and controlled production of samples for small-scale testing. The samples were then used in various experiments to investigate the sensitization of nAl/fluoropolymer composites by charge application, electrical poling, and inert doping. Piezoelectric behavior of the composites resulting from nanoparticle doping and electrical poling was successfully demonstrated by measuring the voltage developed as a result of applied mechanical stress. Drop weight ignition experiments showed that the impact ignition sensitivity of electrically poled samples could be controlled using a strong electric field. In addition, it was demonstrated that the burn rate of nAl/fluoropolymer sheets could be significantly enhanced under the influence of an electric field. Finally, a nAl/THV composite was shown to be susceptible to photoflash ignition. These results demonstrate the potential for using these nAl/fluoropolymer composites as tailored energetic materials and as additives to control the sensitivity of other energetic systems. Thus, proposed future work includes further investigation of the piezoelectric response of the composites under extreme mechanical stress and torsion and the effect of applied external electric fields. In addition, further experiments on burn rate enhancement and the use of the composites as sensitizing additives is also proposed.

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PROBLEM STATEMENT

The effort to realize advanced munitions through the use of high-performance and safe energetic materials has led to the interest in nano-composite energetic materials. A particular class of energetic materials, nano-aluminum/fluoropolymer composites, are of interest due to their high densities and performance-enhancing capabilities in explosive [1], propellant [2,3,4], and pyrotechnic applications [5,6,7]. In particular, the nano-aluminum (nAl)/fluoropolymer system has been demonstrated to exhibit susceptibility to ignition sensitization by means of charge application [8], potentially due to the piezoelectric properties of the fluoropolymer. This feature has direct application to the safety and performance of fielded systems. However, the mechanism through which sensitization is possible was not evident and required further investigation if such a composite is to be deemed feasible for advanced munitions application. It was therefore proposed to characterize and study potential nAl/fluoropolymer systems in an attempt to understand the means by which sensitization can be controlled. However, it was first required to develop a standard procedure for the synthesis of such formulations in order to proceed with a systematic investigation of their ignition and combustion properties. We therefore proposed to develop novel approaches for preparing aluminum/fluoropolymer nano-energetic composites and methods to alter and control their ignition sensitivities without comprising combustion performance. Therefore, the following objectives were proposed: (1) the development of synthesis procedures for nano-aluminum/fluoropolymer composites for the consistent and controlled production of samples for small-scale testing; and (2) the investigation of the sensitization of nAl/fluoropolymer composites by charge application, electrical poling, and inert doping in order to definitively identify the mechanism responsible for sensitization susceptibility.

SUMMARY OF IMPORTANT RESULTS

1. Thermochemical Equilibrium Calculations

Thermochemical equilibrium calculations were performed using the Cheetah 7.0 equilibrium code [9] to examine the theoretical combustion behavior of multiple aluminum/fluoropolymer systems using fluorocarbon binders common to propellant and explosive applications. The equilibrium adiabatic flame temperature calculations were done at constant ambient pressure (1 atm) and are shown in Figure 1 as a function of aluminum content. The three fluoropolymers examined include THV (tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride), PTFE (tetrafluroethylene), and Viton (hexafluoropropylene-vinylidene fluoride) polymers. The monomer empirical formulae for THV, PTFE, and Viton are $C_{2.29}F_{4.33}H_{0.25}$, C_2F_4, and $C_5F_{6.5}H_{3.5}$ respectively. The adiabatic flame temperature trends are highly similar for THV and PTFE due to the similar fluorine-carbon ratio, and the high adiabatic flame temperatures are attributed to the formation of α-AlF_3. The lower adiabatic flame temperature for Al/Viton is due to its higher heat of formation and low enthalpy compensation through exothermic reactions. The low fluorine-carbon ratio and excess hydrogen (relative to THV) reduce the formation of AlF_3 and increase the formation of HF and CF_x, all of which would decrease the adiabatic flame temperature relative to Al/THV. The flame temperatures for all three fluoropolymer systems exhibited a plateau due to the onset of formation of Al_4C_3, which is relatively stable and liberates little energy upon formation relative to the formation of AlF_3 (1.88 kJ/g of aluminum vs. 56.01 kJ/g [10]). The most fluorinated available fluoropolymer is PTFE, where a carbon backbone is saturated with fluorine atoms. However, and as will be discussed later, a thermodynamically stable piezoelectric polymer structure requires the additional presence of hydrogen for the formation of a strong dipole moment, as is the case for both THV and polyvinylidene fluoride (PVDF).

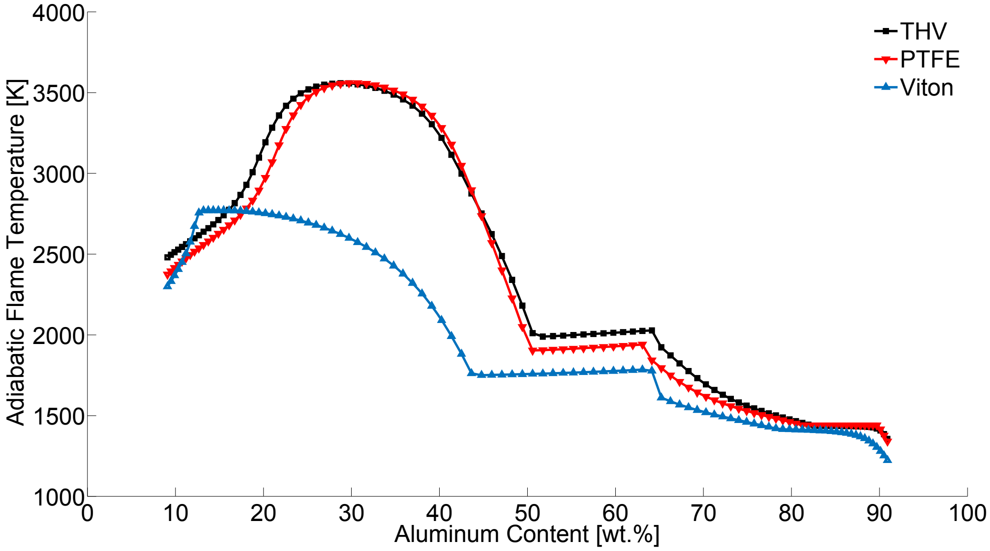

Figure 1. Adiabatic flame temperature of multiple aluminum/fluoropolymer systems.

2. Nano-Aluminum/Fluoropolymer Composite Preparation and Characterization

2.1 Formulation and Preparation

The nano-fuel proposed for the composite systems was 80 nm NovaCentrix nano-aluminum (nAl) with a native alumina passivation shell resulting in 82 wt.% active nAl content. The two fluoropolymers proposed for the investigation were Dyneon™ THV 221AZ, which is a terpolymer of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and vinylidene fluoride (VDF) with the empirical formula $C_{2.29}F_{4.33}H_{0.25}$, and Kynar® polyvinylidene fluoride (PVDF) with the empirical formula $C_2F_2H_2$. These fluoropolymers are known to exhibit piezoelectric behavior due to formation of the electroactive β- and γ-phases of PVDF, which are responsible for a strong dipole moment in the PVDF monomer due to the physical separation and relative electronegativity difference between the hydrogen and fluorine atoms [11]. Different compositions of the nAl/fluoropolymer systems were prepared in one-gram batches using 3-5 mL of various solvents. Several potential solvents were investigated, and the use of a particular solvent depends on the chosen method of deposition and fluoropolymer solubility. Propanone and butanone are active solvents for THV, while dimethylformamide (DMF) is only latent. Further, butanone and DMF are active solvents for PVDF, while propanone is only latent. Therefore, the solvents investigated were propanone, butanone, and DMF. Solvent applicability and sample deposition are discussed in Section 2.2. The batches of nAl/fluoropolymer were prepared in stoichiometric ratios (30/70 wt.% for Al/THV and 22/78 wt.% for nAl/PVDF), accounting for the native passivation shell.

The fluoropolymer-solvent solution was stirred using a magnetic mixer with a stir bar, operating at 600 rpm for 20 minutes in a sealed glass vial to prevent the evaporation of the solvents. The magnetic stirrer was used to accelerate the dissolving of the fluoropolymer. The nAl was added to the mixture and the resulting mixture was then ultrasonically mixed (Branson Digital 450 Sonifier Cell Disruptor with a tapered microtip) at 30% amplitude for 5 minutes. The sonication of the solution was needed to ensure a homogenous dispersion of the nAl throughout the solvent and to reduce agglomerations. The resulting suspension was then used in a variety of different deposition methods as discussed in Section 2.2.

It is known that neat untreated PVDF exists in the α-phase only, which is not electroactive. PVDF requires some electrical or mechanical treatment to induce the metastable electroactive β-phase [11]. Further, it has been reported that, unlike neat PVDF, the β-phase of PVDF in untreated poly(vinylidenefluoride-co-hexafluoropropylene) P(HFP-VDF) is favored simply due to the interference of TFE and HFP on the semi-recrystallization of PVDF [12]. This feature of P(HFP-VDF) motivated the investigation of THV given its superior mechanical properties as a binder relative to PVDF. Two different approaches were investigated to achieve the β-phase of neat PVDF: TiO_2 doping and electrical poling. It is known that the solidification of PVDF under a strong electric field results in the permanent orientation of the previously randomly-oriented polymer chains, resulting in permanent dipole moments and hence the electroactive β-phase and γ-phases of PVDF [12]. Therefore, in the current work neat PVDF was dissolved in DMF and then subject to electrical poling at 10,000 V at 80°C with a 5 cm electrode separation. Further, it has also been demonstrated that the doping of neat PVDF with 5 wt.% nano-TiO_2 resulted in the favoring of the β-phase upon recrystallization [13], which was attributed to the matching of the TiO_2 and β-phase crystal lattice, preventing the transition to the stable α-phase. Therefore, in the current work neat PVDF was doped with TiO_2 (21 nm diameter), and was prepared as described previously. The poled and doped samples were then examined using an x-ray diffraction (XRD) technique (Bruker D8 X-ray powder diffractometer) operating at a scan rate of 2°/min to confirm formation of the electroactive phases.

It is interesting to note that solid composite formulations using THV (nAl/THV, nAl/THV/polybutadiene, and nAl/THV/Sylgard) were also demonstrated, perhaps for the first time, to be susceptible to photo-thermal ignition. The samples were shown to be readily ignitable using a commercial xenon tube flash. The proposed composite therefore presents a new system in the class of photo-thermal sensitive nanoscale reactives [2,14].

2.2 Sample Deposition Methods

Multiple deposition methods were investigated in an attempt to precisely control the thickness, mass, and homogeneity of produced samples. For larger thicknesses, perhaps the simplest approach is casting, which involves pouring the prepared solution into a mold and allowing the solvent to evaporate at ambient conditions. Depending on the solvent, it may also be of practical interest to force quicker evaporation of the solvent at elevated temperatures. Propanone and butanone have high vapor pressures, thus causing the solvent to escape quickly from the drying composite. However, DMF requires nearly 24 hours to evaporate at ambient conditions due to its low vapor pressure; such a time may be reduced by placing the drying composite in an elevated temperature environment (below the melting temperature of the fluoropolymer). Also, it should be noted that temperatures in excess of 100°C may result in adverse porosities due to the forced evaporation, which has been demonstrated to influence mechanical properties of the composite [8]. All of the proposed active solvent-fluoropolymer pairs are appropriate for the casting method. In principle, the casting method may be used to produce thin-layered (< 50 μm) samples, depending on the size of the batch produced and the dimensions of the mold. However, given the practical constraints posed by the size of the ultrasonic mixer and the yield losses (characteristic of nanometric colloidal suspensions) to the container walls, homogenous and consistent deposition can only be achieved for thick (> 50 μm) samples. Therefore, the casting method is limited to producing relatively thick samples. However, while there is a limitation on the lowest thickness achievable, the casting method is suitable for large-batch production of samples.

Alternative methods for finer control of the composite sample thickness were then investigated. The use of a spin-coating apparatus enabled precise control of the sample thickness. It is known that the coating thickness of a material depends on the solids loading of the solution, the angular speeds used for spin coating, the kinematic viscosity of the solution, and the rate at which the solvent evaporates from the composite. It is therefore obvious that a heuristic approach is required for spin coating of the proposed composites. The high vapor pressure of propanone results in difficulties in thickness control of samples, while the low vapor pressure of DMF precludes its use for high-speed spin-coating applications, leaving only butanone as a suitable solvent. Using a standard two-stage spin-coating apparatus, and for thin coatings (< 20 μm) of the nAl/fluoropolymer using butanone, the following guidelines were established: minimum angular speed of 500 rpm, maximum angular speed of 1100 rpm, with 60 second first-stage intervals and varying (1-60 second) second stage intervals. While the spin coating method allows for precise control over the sample thickness, it only results in low sample yields due to the excessive loss of material during the spin-coating process. Also, the homogeneity (nAl dispersion within the fluoropolymer matrix) depends on the solids loading used and decreases with increasing solids loading as a result of nanofuel separation.

Finally, the selective deposition of the composite using piezoelectric inkjet printing was considered. This method would theoretically allow for exact control of both thickness and mass of samples. While the plausibility of such an approach was demonstrated by printing 2% solids loading nAl/THV using butanone, such a procedure is still currently under development and requires optimization with respect to the solution solids loading.

2.3 Sample Yield and Testing Preparation

Sample preparation was performed such that uniform and consistent samples may be used for a variety of sensitization experiments including drop weight and CO_2 gas laser ignition experiments. Preliminary ignition testing using a drop weight impact apparatus demonstrated difficulty in achieving repeatable ignition of thin-layered samples prepared using the spin coating apparatus, possibly due to quenching as a result of rapid heat dissipation. However, it was possible to achieve repeatable ignition through high-flux heating using the CO_2 laser. As a result, while the spin-coating method was optimized, it was ultimately abandoned for most of the experimental investigation since comparable results are required from both the laser ignition and drop weight ignition. Therefore, it was concluded that testing would be performed on thicker (> 50 μm) samples prepared using the casting method described in the previous section. Individual samples were prepared by dividing the dried film into circular samples with diameters of 0.6 cm or 0.9 cm, and the individual samples were weighed to analyze the mass distribution. The mass distribution for multiple fuel-rich batches (84 samples) of 43/57 wt.% mass distributions is shown in Figure 2.

The slow evaporation of the solvent (butanone) during casting results in some settling of the nAl, producing variations in density towards the edge of the mold. Therefore, the samples made from the prepared batches will have some mass distribution. The distribution of the samples masses was determined in order to exclude inhomogeneous samples and to define an operating range of masses. Samples with masses that were outside the range of 30-35 mg from visibly exhibited significant variations in density (either excess THV or nAl) were mostly excluded from testing.

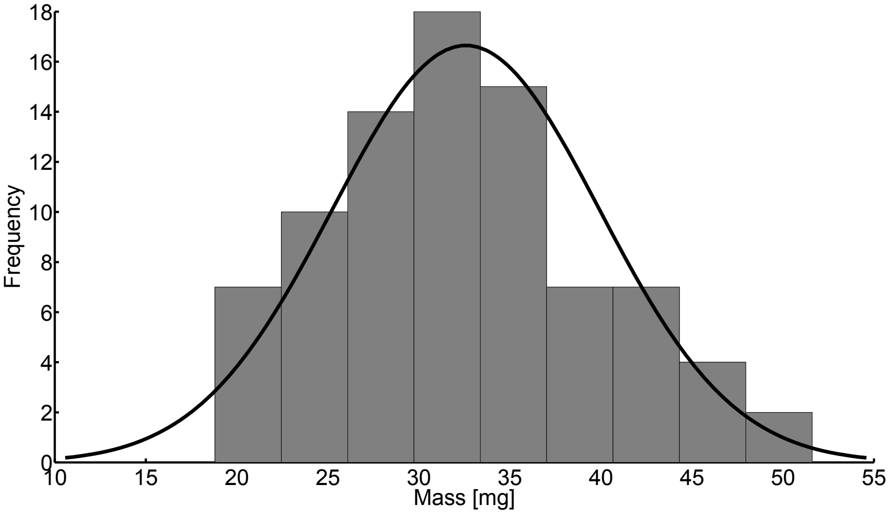

Figure 2. Multiple batch mass distribution (N=84) of 43/57 wt.% nAl/THV.

2.4 Sample Characterization

Characterization of the nAl/fluoropolymer systems was performed using simultaneous differential scanning calorimetry and thermogravimetric analysis (TA Instruments SDT Q600 V20.9) operating at a 20°C/min heating rate and a 100 mL/min mixture flow of oxygen/argon (20/80 vol.%) over a range of 50-800°C. Surface morphology was examined using scanning electron microscopy and energy dispersive spectroscopy (FEI Nova 200 NanoLab DualBeamTM-SEM/FIB). The surface reflection characteristics were also examined using spectrophotometry (PerkinElmer Lambda950 UV-VIS-NIR spectrophotometer) in an attempt to explain the high susceptibility to photoflash ignition.

The results of the differential scanning calorimetry for nAl/THV and neat THV are shown in Figure 3. It is known that the decomposition of PTFE [15] and PVDF [16] liberate radical fluorinating species that attack the native Al_2O_3 passivation shell to produce AlF_3. The previously passivated nAl core is then exposed to oxidation in a reaction termed the pre-ignition reaction (PIR). The onset of the PIR corresponds to the onset of the decomposition of fluoropolymer, and the main oxidation exothermic peak is triggered by the PIR and is indicated by the rapid increase in the heat flow gradient. The high exothermicity of the reaction is attributed to the rapid consumption of the nAl due to its large specific surface area, which facilitates its rapid and complete combustion as indicated by the absence of a strong endothermic peak at 660°C, the nominal melting point of Al. However, we also note that the magnitude of the exothermic peaks (heat liberated) is consistent with the oxidation of nAl [17], rather than its fluorination, which suggests that the combustion of the samples is an oxidation process triggered by the PIR.

Thermogravimetric analysis of the neat THV showed 100% weight loss at the onset of decomposition, which is a result of the liberated CF_x and HF gaseous species. Further, the thermogravimetric analysis of nAl/THV showed only an 82% weight loss, which suggests the presence of solid combustion products, mostly Al_2O_3 and solid C.

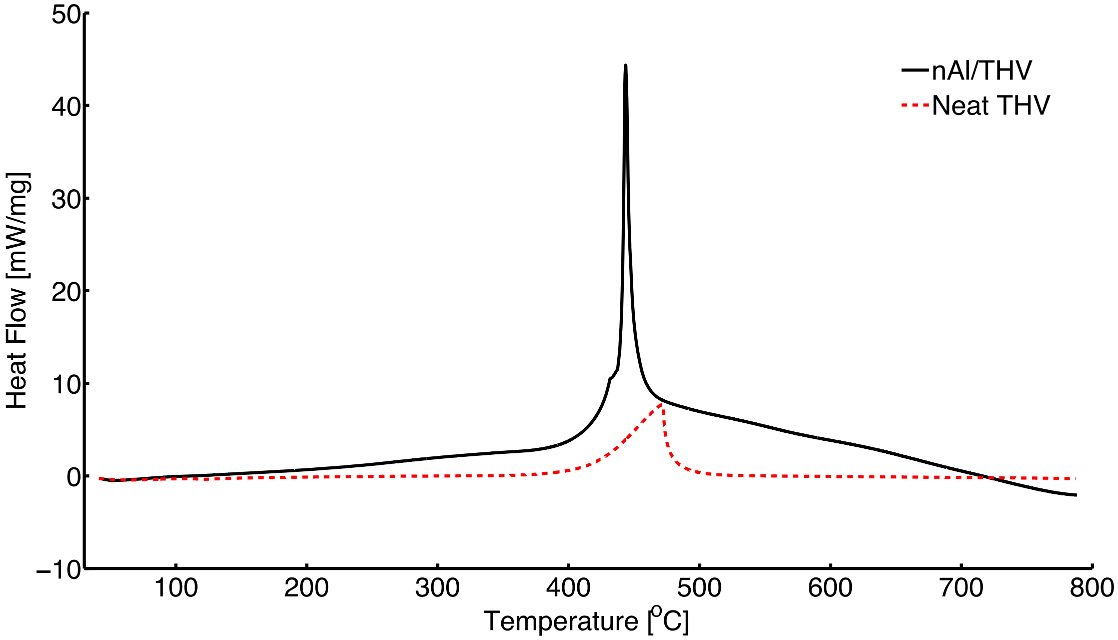

Figure 3. Differential scanning calorimetry (positive exotherm) for nAl/THV (30/70 wt.%) and neat THV (20/80 wt.%) in O_2/Ar.

An electron micrograph of nAl/THV particles is shown in Figure 4, which shows the surface morphology characteristic of the composite. Further, a brief energy dispersive spectroscopic investigation, shown in Figure 5 revealed a homogeneous distribution between the nAl and its fluoropolymer coating. Finally, a brief spectrophotometric investigation revealed a low reflectance (relative to a reference white blank) of the nAl/THV composite across the wavelength range between 300 nm and 1800 nm, as shown in Figure 6. The commercial photoflash used in the ignition tests (Nikon SB-24 Xenon photoflash) is known to emit broadband radiation in the visible and near infrared ranges [18], and the emitted radiation is therefore easily absorbed by the surface of the nAl/THV composite, which perhaps explains the high sensitivity to photoflash ignition.

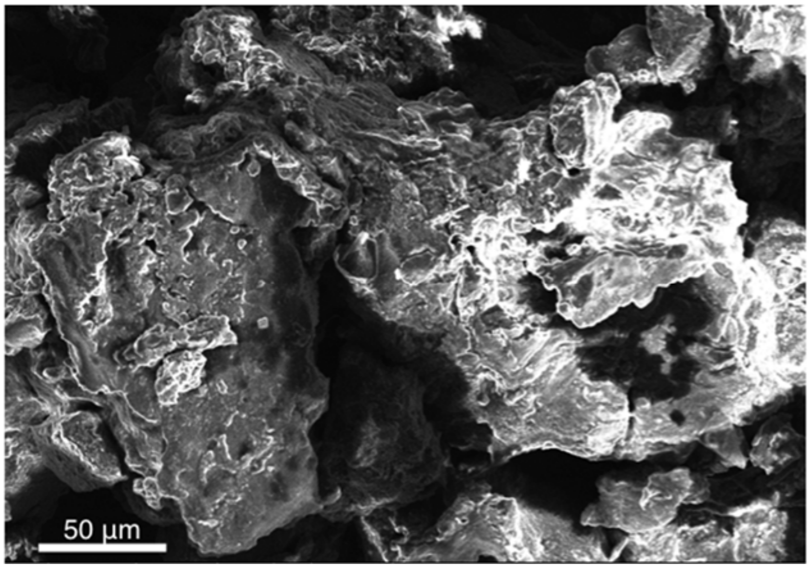

Figure 4. Electron micrograph of nAl/THV composite particles.

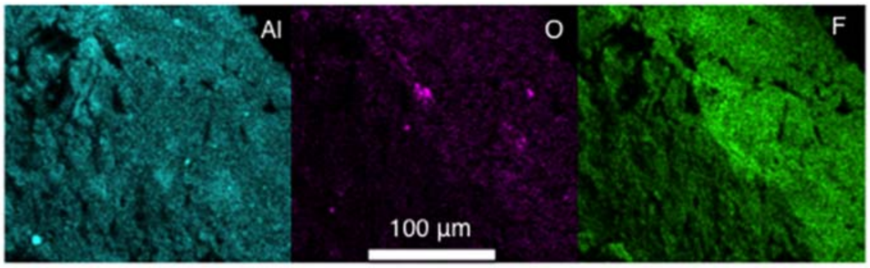

Figure 5. Element map using energy dispersive spectroscopy on nAl/THV composite.

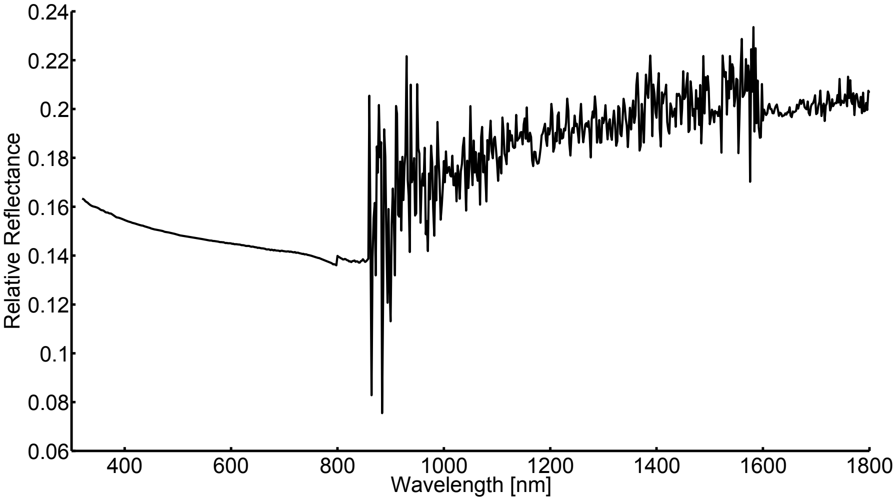

Figure 6. Relative reflectance (relative to white blank reference) of nAl/THV film.

3. Sensitization and Combustion Experiments

3.1 X-Ray Diffraction and Voltage Response

Treated and untreated samples of aluminized and neat fluoropolymers (THV and PVDF) were inspected using x-ray diffraction (XRD), and their voltage response to mechanical stress was also measured in order to confirm β-phase formation. The XRD results, shown in Figure 7, indicate the successful formation of the metastable β-phase in PVDF using both the electrical poling and TiO_2 doping methods, both of which result in the preferential orientation and close packing of the molecular chains. The results suggest that doped and electrically poled samples should exhibit some piezoelectric behavior due to the presence of the electroactive metastable β-phase of PVDF.

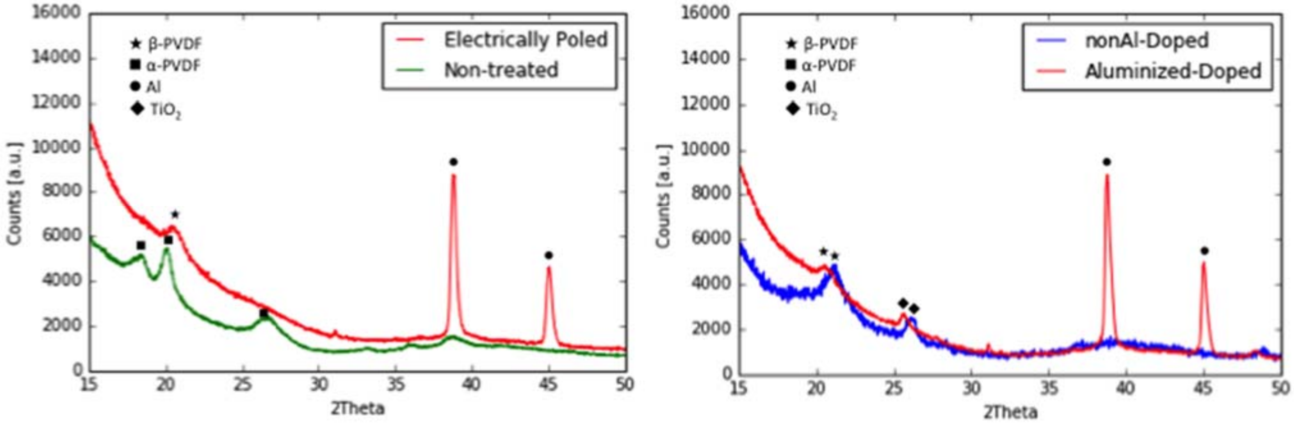

Figure 7. X-ray diffraction results for untreated PVDF, poled nAl/PVDF, nAl/TiO_2/PVDF, and TiO_2/PVDF.

To confirm piezoelectricity, a variety of treated and untreated samples were placed between electrodes and subject to a constant controlled mechanical stress, and the voltage response was measured using an oscilloscope. The maximum of the voltage response for each system is shown in Figure 8. For reference, a negative control reference sample recorded 0.043V and a commercial poled PVDF gauge recorded a response of 0.91V. Additionally, we note that all of the samples that were shown to contain the β-phase resulted in a positive voltage reading upon sustaining mechanical stress, as shown in Figure 8. As shown in Figure 8, the introduction of nAl into a PVDF matrix results in no significant voltage response (indistinguishable from the negative control reference), which is to be expected given the prevalence of the α-phase in PVDF. Further, it appears that the casting of untreated THV does result in some β-phase formation due to the interference of HFP and TFE with the recrystallization of PVDF to the stable α-phase. Also, it is obvious that the introduction of nAl does not promote the formation of the β-phase in neat PVDF, likely due to the mismatch between its lattice constant and that of the β-phase in PVDF. Conversely, it appears that the introduction of nAl into an untreated THV matrix does promote some β-phase formation, possibly due to its promotion of the interference of the HFP and TFE in PVDF recrystallization. However, when TiO_2 is introduced along with nAl into THV, the previous effect is overshadowed by the reduction in the TiO_2 dispersion homogeneity, which has a net result of inhibiting β-phase formation. Moreover, we notice that the nAl/TiO_2/PVDF has a greater voltage response than its nAl/TiO$_2$/THV counterpart, due to the relative scarcity of PVDF in the latter. Finally, we note the relatively large voltage response of the poled nAl/PVDF (denoted E-nAl/PVDF), which is superior to all of its aluminized counterparts.

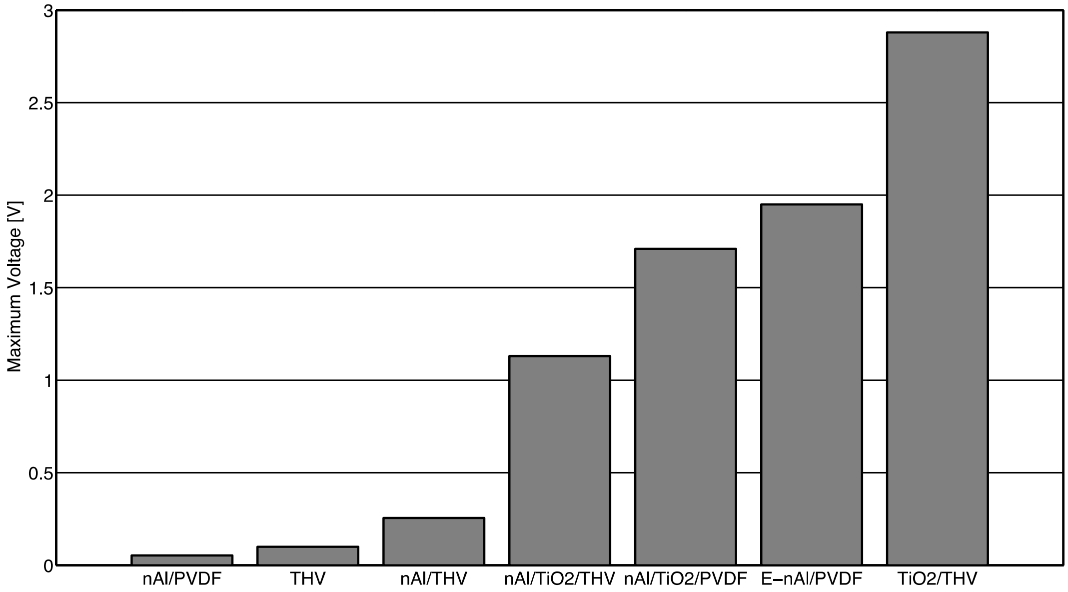

Figure 8. Maximum voltage response due to mechanical stress for multiple systems (negative reference of 0.043V).

The average breakdowns of untreated nAl/THV and nAl/PVDF were determined by applying an electric field across the composite samples and determining the level at which ignition occurs. The voltage ignition threshold, as a function of sample mass, is shown in Figure 9. A simple correlation analysis reveals a Pearson correlation coefficient of ρ= 0.32, indicating a weak correlation between mass and ignition threshold. The weak correlation may be due to small variations in sample thickness or average nAl particle separation, either of which would influence the dielectric breakdown strength. We note that a similar investigation of nAl/PVDF was done, which revealed a breakdown threshold of 2.2 kV. The determined voltage ignition thresholds were then used to investigate the influence of a strong electric field (with applied voltages near the breakdown voltage) on the combustion behavior of treated and untreated samples.

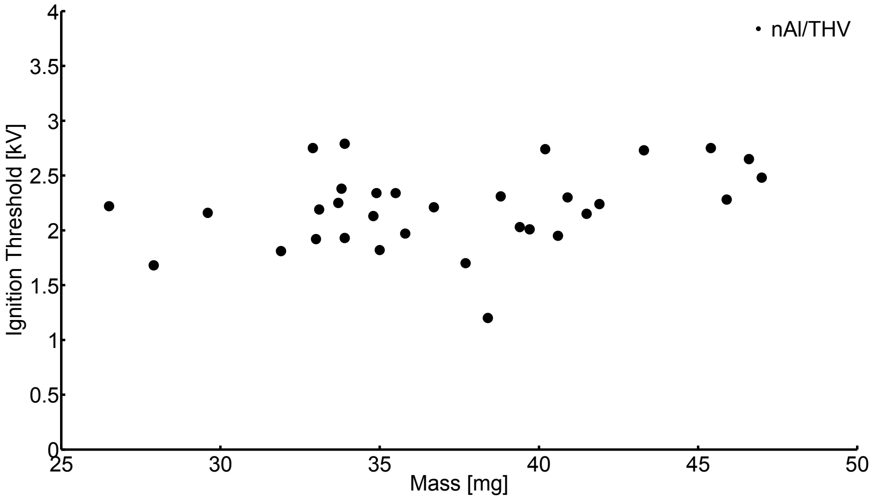

Figure 9. Voltage ignition threshold of nAl/THV as a function of sample mass.

3.2 *Drop Weight Impact and Friction Sensitivity*

Ignition sensitivity thresholds for various stimuli were determined using a statistical d-optimality-based sensitivity test, developed by Neyer [19], which has wide application in energetic material and explosive sensitivity testing. In the plots in this section, the upper bound of ignition failure is shown in red while the lower bound of ignition success is shown in green. The ignition threshold value to any stimulus is defined as the value around which the lower and upper bounds converge

First, the influence of TiO_2 doping on the drop weight impact ignition threshold of nAl/PVDF was investigated. The setup included a 5 kg drop weight hammer that was incident on a plunger and onto the samples from a variety of heights as described elsewhere [8]. As seen in Figure 10, the threshold for untreated nAl/PVDF is 27.6 inches, while that of nAl/TiO_2/PVDF was 19.7 inches. The results suggest that doping nAl/PVDF with nano-TiO_2 results in increased sensitivity (lower impact energy), but is inconclusive as to whether the sensitization resulted from the formation of the β-phase of PVDF or the increased friction sensitivity due to the presence of additional inert nanoparticles. As noted previously, the TiO_2 particles were roughly four times smaller than the nAl used in this work.

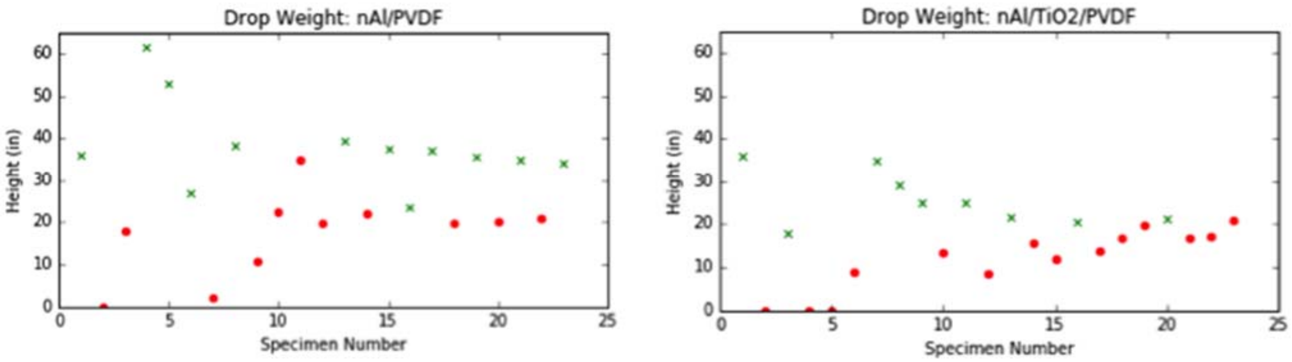

Figure 10. Drop weight impact sensitivity of nAl/PVDF and nAl/TiO_2/PVDF.

A complementary standard friction sensitivity test was also conducted in an attempt to confirm the drop weight impact results, and the results are shown in Figure 11. The friction sensitivity tests were performed using a standard BAM friction apparatus. The force ignition threshold for the untreated nAl/PVDF was 152 kg, while that of nAl/TiO_2/PVDF was 136 kg, which indicates increased friction sensitivity by doping. We note that both the PVDF β-phase and the mechanical inclusion of TiO_2 nanoparticles (increased internal friction) were expected to influence the ignition sensitivity of the composite. However, we could not isolate their relative contributions to ignition sensitivity, which necessitated the use of poled samples instead of doped samples in order to isolate the effect of the β-phase. Hence, the drop weight impact thresholds of untreated nAl/PVDF and poled nAl/PVDF were similarly investigated, and the results are shown in Figure 12.

The untreated nAl/PVDF appears to be much more sensitive than its poled counterpart, with thresholds of 15.68 inches and 29.27 inches, respectively. That is, poling the nAl/PVDF samples to orient the PVDF polymer chains actually reduces its impact sensitivity, which may be explained by simple mechanical arguments. In the case of the untreated samples the polymer chains are randomly oriented, whereas they are preferentially aligned in the case of the poled samples. Hence, it is suspected that such a preferential alignment, in the case of the poled samples, inhibits the conversion of kinetic impact energy to internal energy through friction, whereas the randomly oriented chains in the untreated samples facilitates such dissipation.

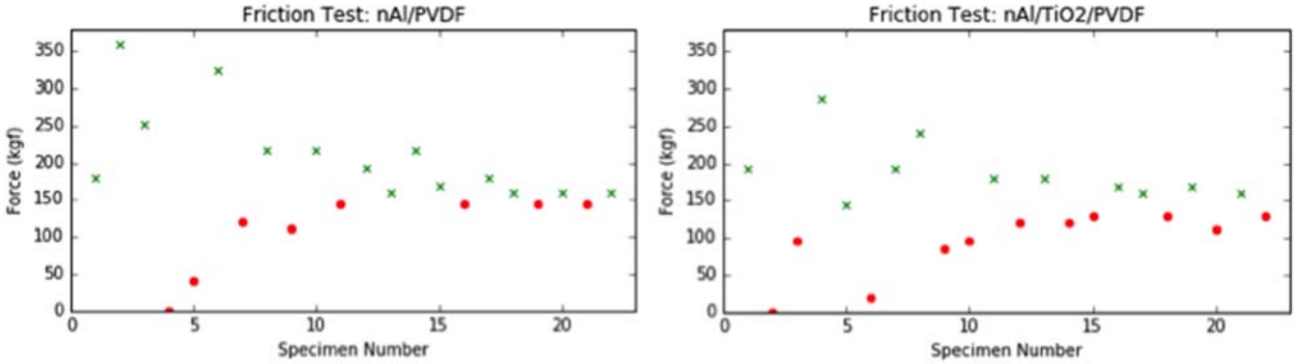

Figure 11. Friction sensitivity of nAl/PVDF and nAl/TiO_2/PVDF.

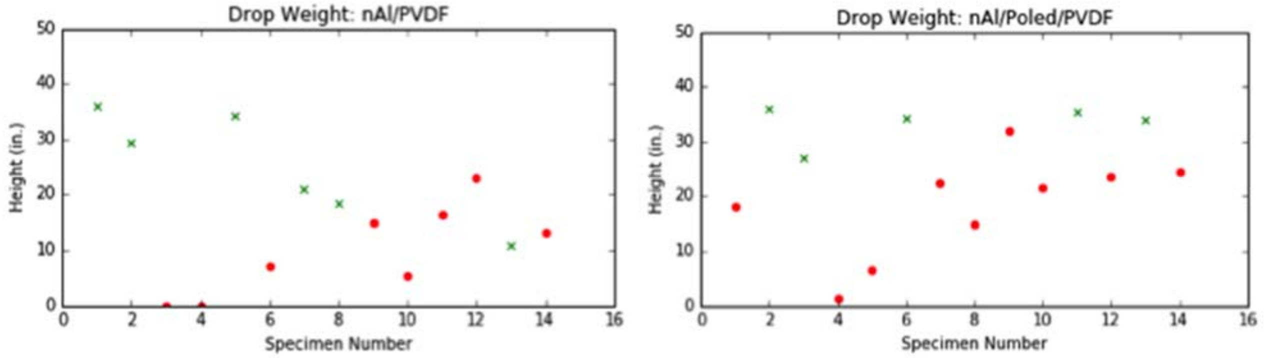

Figure 12. Drop weight impact sensitivity of untreated nAl/PVDF and poled nAl/PVDF.

Further, the influence of an applied electric field on poled nAl/PVDF samples was investigated. It was expected that the applied field would enforce or undermine the previously achieved polarization (by electrical poling) depending on the physical orientation of the sample with respect to the direction of the applied electric field. Positive alignment of the poled sample corresponds to the sample being oriented in the direction of the applied field, and a negative alignment for the converse. As seen in Figure 13, negatively aligned samples exhibited increased sensitivity relative to their unpoled counterpart (29.78 inches and 25.0 inches respectively). It is hypothesized that the positive alignment of the poled sample enforced the polymer chain alignment, which has been previously argued to decrease the conversion of impact kinetic energy to internal energy by means of friction. Conversely, the negative alignment of the poled samples facilitates the disruption of the polymer chain orientation, thereby increasing the conversion of impact energy to internal energy through friction. To independently confirm, five samples of poled nAl/PVDF were placed in positive orientation and five others were placed in a negative orientation with respect to the applied electric field. The samples were then subjected to drop weight impact at a fixed height of 26 inches (just above the previously determined threshold). The negatively oriented samples ignited in 100% (5/5) of the tests, whereas the positively oriented samples ignited in only 20% (1/5) of the tests, supporting the aforementioned influence of the sample orientation on ignition sensitivity.

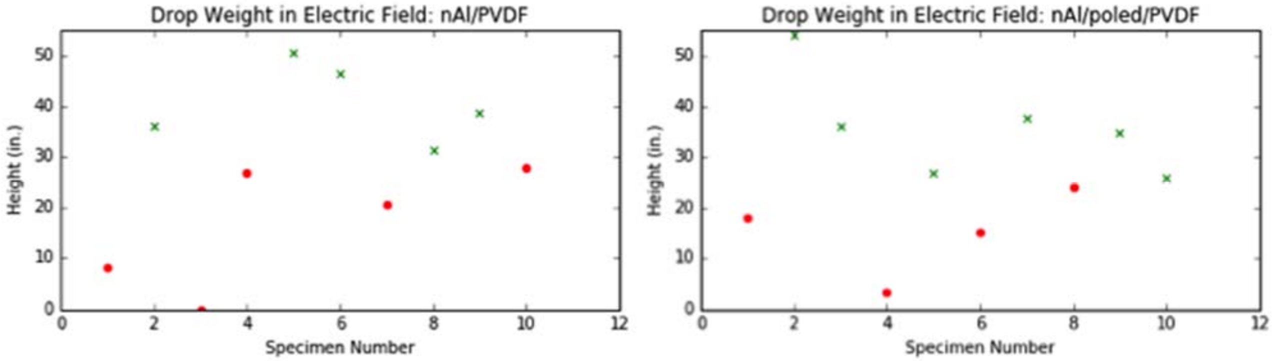

Figure 13. Drop weight impact sensitivity of charged (2000V) untreated nAl/PVDF and poled nAl/PVDF (negative alignment).

3.3 CO$_2$ Laser Ignition

Laser ignition thresholds and ignition delays were measured for treated and untreated samples using a Coherent 80W CO$_2$ 10.6 μm laser. Unlike drop weight impact and friction sensitivity testing, the transfer of the laser beam energy occurs directly to the reactants, regardless of the nature of the local polymer chain orientation (given the same surface absorptivity). Whereas in the case of drop weight impact and friction sensitivity, the mechanical orientation of the polymer chains, which is function of the phase of PVDF and the dopant nanoparticles, influences the conversion of impact kinetic energy to the sample internal energy by means of friction. As seen in Figure 14, the laser power ignition threshold of the untreated nAl/PVDF and poled nAl/PVDF is practically identical (13.32W and 12.77 ± 0.917W, respectively).

To investigate the influence of the application of an external electric field on the ignition energy of the nAl/fluoropolymer samples, measurements of laser ignition delay (time to first light) were conducted using high-speed videography (Vision Research Phantom v7.3, Nikon 200mm f/4 AF-D Macro). The results of these tests are shown in Figure 15. It is clear that the application of an external electric field has no effect on the laser ignition delay (and hence ignition energy), which follows from the energy conversion arguments presented previously.

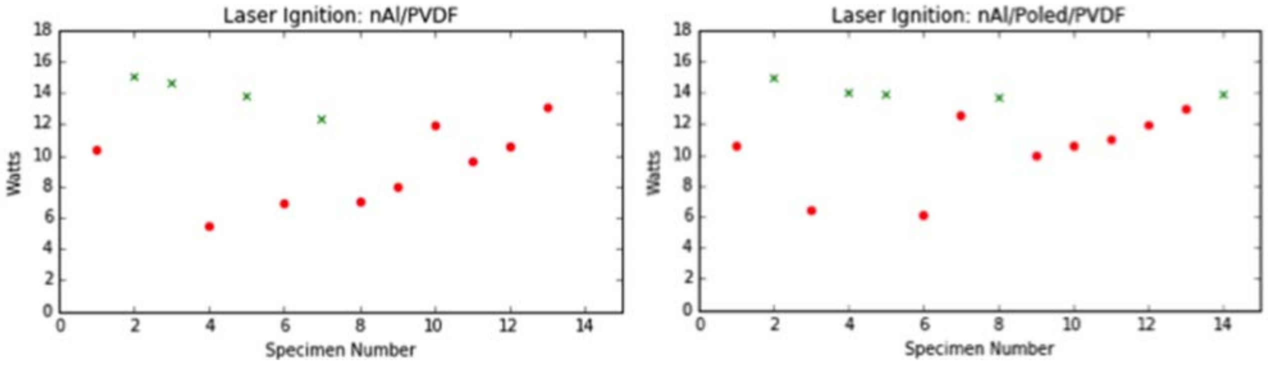

Figure 14. Laser ignition power threshold for untreated nAl/PVDF and poled nAl/PVDF.

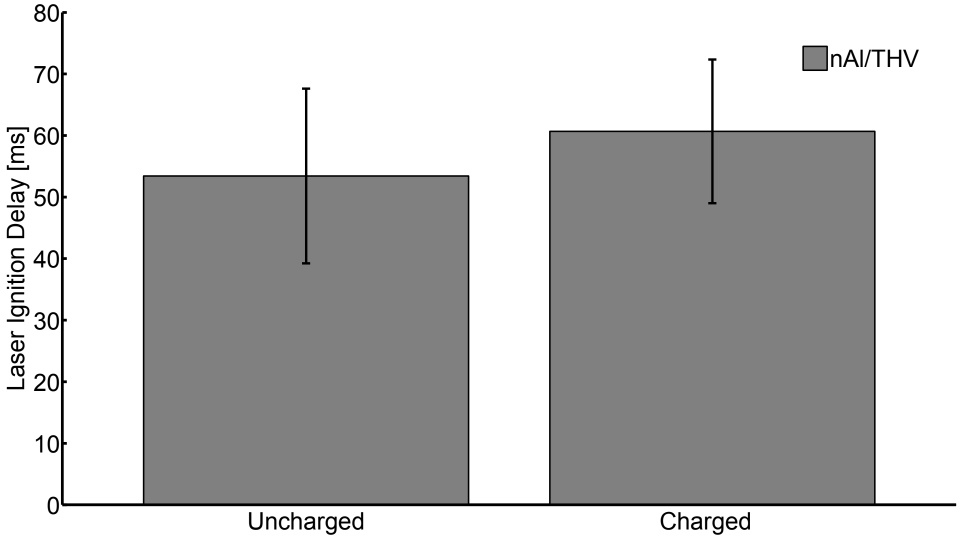

Figure 15. Laser ignition delay of uncharged and charged (1800V) nAl/THV composites.

3.4 Burn Rate Enhancement

Finally, the influence of an externally applied electric field on the burn rate of sheets of nAl/THV was investigated. Sheets of nAl/THV were placed between conductive copper electrodes, after which an external voltage of 1800V was applied and the samples were ignited from one end. The average burn rates were determined using high-speed videography and are shown in Figure 16. The results suggest that applying an external electrical field increases the burn rate of the samples substantially. It is known that increasing the net thermal conductivity of a sample, by means of a thermal conduit, increases the burn rate of composite samples [20]. However, since copper electrodes surrounded both of the uncharged and charged samples, the burn rate enhancement cannot be attributed to the increase in thermal conductivity. Instead, it is suspected that the heat liberated from the reaction zone may have been transferred to unburned portions, lowering the dielectric strength. This resulting in premature ignition downstream of the burning surface due to dielectric breakdown. Hence, the application of a strong electric field, with a voltage near the ignition threshold of that of the composite sample, appears to result in burn rate enhancement.

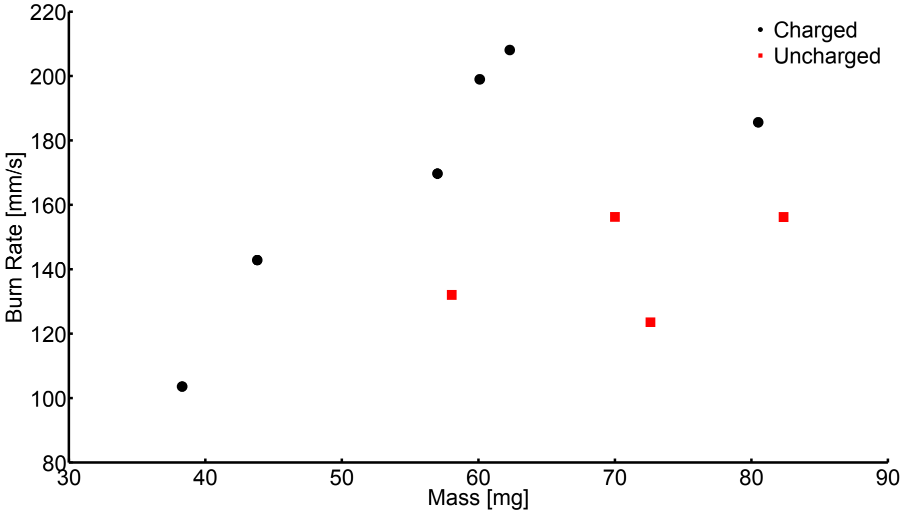

Figure 16. Burn rates of sheets of charged vs. uncharged nAl/THV.

CONCLUSIONS AND FUTURE WORK

Novel nano-aluminum/fluoropolymer energetic composites were proposed and investigated in an attempt to precisely control and tune their ignition sensitivities. We proposed methods to synthesize nano-aluminum/fluoropolymer composite films and demonstrated their piezoelectric behavior that resulted from nanoparticle doping and electrical poling. We have demonstrated the ability to control the drop weight impact ignition sensitivity of electrically poled samples using a strong electric field, due to the preferential alignment of the polymer chains in the β-phase of PVDF. However, we have not yet demonstrated a utilization of the piezoelectric behavior of the composites without the use of an external electric field, but this may not be very difficult to accomplish. Therefore, we propose further investigation of the composites under extreme mechanical stress through high-velocity impact, which may be sufficient to initiate dielectric breakdown through the sample due to large charge separation. We further propose the investigation of the dielectric breakdown and piezoelectric response of the proposed composites under torsional stress, in order to isolate the influence of shear stress on the reactivity of the composites. We will also conduct similar tests (impact, friction, torsion) using nAl/THV samples since this formulation was previously shown to be sensitized by applied electric fields [8].

We have also demonstrated the burn rate enhancement of nAl/fluoropolymer sheets under the influence of a strong electric field, but further investigation is required in order to isolate the mechanism responsible for such behavior. The ability to control the burn rate of such composites, without the use of additional inclusions, would allow for precise control of corrosive (e.g. HF) gaseous product liberation rates without hindering performance. The control over gas liberation rates may be of interest for certain applications including bioagent defeat. Finally, we have also demonstrated a nAl/THV composite that is susceptible to photoflash ignition. This was explored further by leveraging AFOSR funded work. Hence, the proposed composite may be used to alter the reactivity of other inherently insensitive energetic systems and their susceptibility to optical ignition. Further investigation is required to determine the introduction routes of the proposed composites into other high-performance energetic systems. The precise control of the ignition sensitivity of the proposed energetic composites, without the use of an external electric field, would have a strong influence on the safety and performance of advanced munitions.

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