

Ignition and Reaction Analysis of High Loading Nano-Al/Fluoropolymer Energetic Composite Films

Jeffery B. DeLisio¹, Chuan Huang², Guoqiang Jian¹ and Michael R. Zachariah^{3*}
University of Maryland, College Park, MD, 20742

and

Gregory Young⁴
Naval Surface Warfare Center – Indian Head Division, Indian Head, MD, 20640

*Corresponding author: mrz@umd.edu

With the recent implementation of nano sized metal powders into energetic composites such as solid rocket propellants, incorporating metal nanoparticles with high mass loading in the propellant has become an issue. In this work, an electrospray deposition technique was employed to increase particle loading of nano aluminum (n-Al) and demonstrate the potential of the fluoropolymer, polyvinylidene fluoride (PVDF), as an energetic binder. A mass percentage of 50 % n-Al in PVDF was determined to have the optimal combustion qualities when ignited in air. The Al/PVDF energetic nanocomposite film morphologies were analyzed using scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). Combustion characteristics of the film were analyzed using thermogravimetric analysis/mass spectrometry (TGA/MS) and temperature jump time of flight mass spectrometry (T-jump TOFMS). Ignition temperatures were determined at various pressures in air and argon environments.

I. Introduction

ALUMINUM is commonly used as a fuel in solid rocket propellants due to its various desirable combustion characteristics.¹ Nano sized aluminum particles can, in some cases, further increase these desirable properties and are beginning to be used in various applications primarily due to its increased specific surface area and faster oxidation rates. For propellant applications, aluminum is employed with a polymer binder, which itself may have reactive properties. Among various polymer based energetic binders used in solid propellants, fluorine containing polymers have been able to give the propellant sufficient mechanical integrity as well as enhance its energetic properties.² The reaction induced fluorination of aluminum has been studied and has a calculated energy density greater than that of the oxidation of aluminum on a kilojoule per gram basis. Formation of aluminum fluoride (AlF₃) relative to alumina (Al₂O₃) releases about 80 % more energy per unit mass than oxidation of aluminum (55.7 kJ/g and 31 kJ/g, respectively).³

Fluoropolymers have been studied and employed in a wide variety of energetic compositions as coatings, binders, and oxidizers.⁴ Polytetrafluoroethylene or PTFE (Teflon) has been readily used in energetic formulations due to the high density of fluorine atoms within the polymer.⁵ One major issue when trying to employ PTFE as a binder is the polymer's solubility. A similar polymer, polyvinylidene fluoride (PVDF), does not have this solubility issue and, although not as high as PTFE, still contains a relatively high density of fluorine atoms. PVDF, which contains 59.4 % fluorine by mass, has high mechanical strength, excellent thermal stability and chemical resistance, and has been previously demonstrated to be an efficient binder.⁶

¹ Graduate Research Asst., Chemistry and Biochemistry, 0107 Chemistry Building.

² Visiting Researcher, Chemical and Biomolecular Engineering

³ Professor, Chemical and Biomolecular Engineering and Chemistry and Biochemistry, 2113 Chemical and Nuclear Engineering Building.

⁴ Research Scientist, RDT&E Department.

The purpose of a binder in an energetic composite is to give the fuel mechanical integrity, but should also contribute desirably to the energetic properties of the fuel.^{7,8} Typical energetic binders used in past have been epoxy, nitrocellulose, and various fluropolymers.^{9,10,11} One major issue when using the previously discussed nano aluminum (n-Al) in an energetic composite is achieving high mass loading of the reactive components. This can be very challenging in part due to the rapid increase in viscosity of the polymer melt upon addition of high surface area nanomaterials that makes casting virtually impossible.^{12,13}

In this study, electrospray methods were employed to create high mass loadings of n-Al in an energetic polymeric film. Electrostatic spray deposition (ESD) has been proven to be an effective method for the deposition of films with thicknesses on the nano or micro scale.^{14,15,16} In the ESD process, a liquid solution is charged by passing it through a small nozzle electrically connected to a high voltage. Charges that build up on the surface create a columbic driven hydrodynamic instability that overcomes the surface tension of the solution, resulting in the formation of small, charged monodisperse droplets. To create these thin films, the fine droplets are deposited to a substrate to form uniform solid films following solvent evaporation. The ESD technique can conveniently control the thickness, morphology and uniformity of a film by adjusting the solution concentration, flow rate and applied voltage and is also performed at ambient temperature under atmosphere pressure.

Al/PVDF films with different n-Al mass loadings were made using various weight percentages of Al to PVDF. A very small percentage of ammonium perchlorate was added to decrease the droplet size as discussed later in this paper. The film's optimal composition was determined and characterization using SEM and TGA/MS was performed.

The Al/PVDF composite was analyzed using a modified temperature jump time of flight mass spectrometer (T-jump/TOFMS).¹⁷ Rapid heating is used to replicate the combustion process more accurately than when using slower heating rates.¹⁸ When the rapid heating is preformed inside the TOFMS, the combustion process may be more thoroughly understood by examining the spectra at different times during combustion. The temperature of the wire can also be determined for any given time adding to the overall understanding of the energetic properties of this material. This technique will allow us to study the decomposition, ignition and combustion in a time resolved manner of these polymer composites. The ignition temperature was also measured at various pressures in air and in a pure argon atmosphere.

II. Experimental

A. Materials

Aluminum nanopowders (Al-NPs) (ALEX, 50 nm) used in this work were purchased from Argonide Corporation. The active Al was 70 % by mass determined by thermogravimetric analysis (TGA). Polyvinylidene fluoride (Mw = 534.000) (PVDF), dimethylformamide (DMF) (99.8 wt %) and ammonium perchlorate (AP) (99.8 wt%) purchased from Sigma-Aldrich were directly used as received.

B. Precursor preparation

Typically, 100 mg mixtures of n-Al and PVDF powders with an added 2.0 mg of AP were dissolved in 1.0 mL of DMF solvent. The mixture was first stirred with a magnetic stir bar for 2 hours to dissolve the PVDF, sonicated for 1 hour in a Branson 5510 ultrasonicator, and then stirred again for 24 hours.

C. Electrospray deposition

This method employed a dual spray system using 2 syringe pumps operating with a feed rate of 1.5 mL/hr. A 5 mL syringe on each syringe pump was connected to 23 gauge (ID: 0.43 mm, OD: 0.63 mm) stainless steel needles using PTFE tubing. The two needles were fixed 1 cm apart from each other and 5 cm away from the substrate. A 20 kV differential was set between the needles and the substrate using two high voltage supplies with +10 kV on the needles and -10 kV on the substrate. A rotating drum wrapped in aluminum foil was used as the substrate as depicted in the schematic in Figure 1. The electrospray setup was also modified to coat a thin platinum wire (0.003" diameter) approximately 15 mm in length to be used in the T-jump analysis.

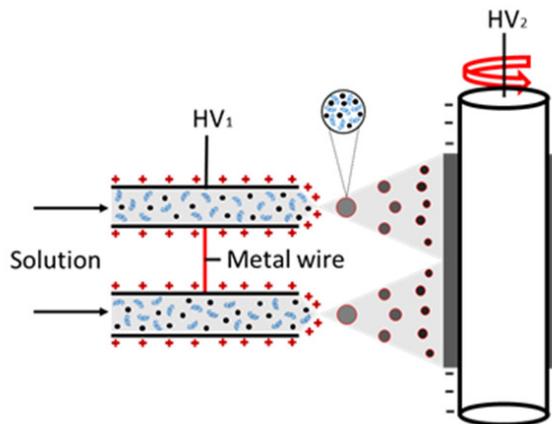


Figure 1. Electrospray deposition of Al/PVDF film setup.

D. Characterization

High-speed video was taken using a Phantom v12.0 digital camera running Phantom 692 software. The videos were recorded at 67000 frames per second. Ignition time and temperature were then determined from the recordings and T-jump data.

The surface morphologies and thickness of the film were characterized using a scanning electron microscope (SEM, Hitachi, Su70 FEG-SEM) equipped with energy dispersive x-ray spectroscopy (EDS). For cross-sectional images, samples were first fractured in liquid nitrogen and then sputtered with carbon.

Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analysis were performed on a SDT Q600 (TA instruments) under flowing nitrogen (50 mL/min). 2-3 mg samples were placed into an alumina pan, and heated from room temperature up to 900 °C at a rate of 20 °C /min.

Temperature jump time of flight mass spectrometry (T-jump TOFMS) was performed using a previously described home-built instrument. Samples were pipetted or electrosprayed onto a 0.003” diameter platinum wire for use in the TOFMS and for ignition temperature tests respectively. The platinum wire was heated with a heating rate of approximately 5×10^5 K/s in these experiments for approximately 3 ms. A sampling rate of 100 μ s per spectrum (10 kHz) was used to capture the progress of the reaction with 95 spectra obtained post-triggering for each run. The data was recorded using 500 MHz digital oscilloscope and transferred to a PC for further analysis.

Ignition temperature tests were performed using rapid heating of a platinum wire (0.003” diameter) coated with an electrosprayed Al/PVDF film approximately 3-5 mm in length inside of a chamber pressurized to a known pressure. High speed video was taken to determine the time when ignition occurs. This time is then correlated to the temperature of the platinum wire at that specific time as described previously.

III. Results and Discussion

In preliminary work, high speed video was taken to analyze the combustion of Al/PVDF polymer composites to determine the optimum equivalence ratio in both air and argon environments at atmospheric pressure. A series of polymer composites were tested with equivalence ratios ranging from 0.25 to 4 (Al/PVDF). The fuel rich equivalence ratio of 2 performed significantly better than all other mixtures in air. Images from the high speed video of burning in air, argon, and vacuum of an electrosprayed Al/PVDF film onto a platinum wire can be seen in the figure below. After determining the optimum equivalence ratio for combustion in air at 1 atm, a 50 % Al to PVDF by mass composition was chosen for further testing.

The 50 % by mass Al/PVDF film was completely

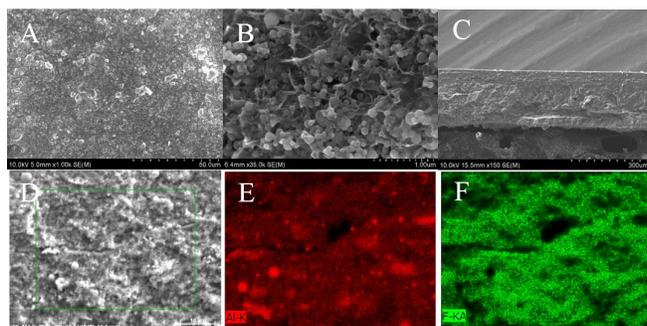


Figure 3. Low magnification (A), surface morphology (B), and cross section (C) SEM images of 50 wt. % Al/PVDF film. EDS scan of film surface (D) showing aluminum (E) and fluorine (F) content.

when it is electrosprayed. This is attributed to the scaling law, which states that the droplet diameter is approximately equal to $K^{-0.33}$, where K is the electrical conductivity of the solution.¹⁹

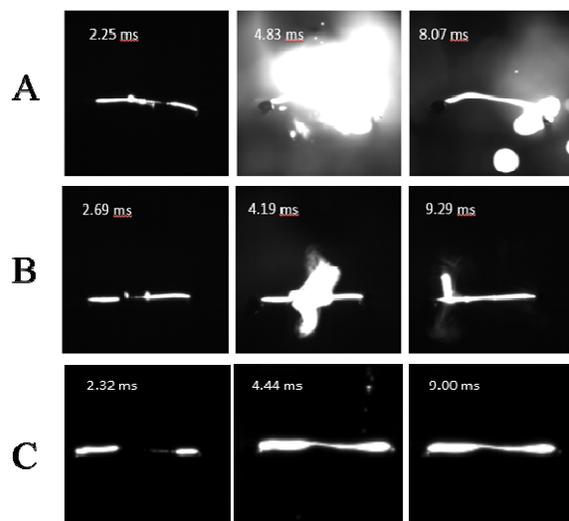


Figure 2. Rapid heating of platinum wire coated with Al/PVDF in air (A), argon (B), and vacuum (C).

removable from the substrate it was electrosprayed onto. Low magnification SEM images of the film show that it is crack-free and smooth. Images of the surface morphology along with the cross-section of the film were taken as shown in Figure 3. EDS scans show the homogeneity of the n-Al and PVDF within the film as seen in Figure 3. The particles are well dispersed within the polymer matrix. The homogeneity of the film can be partly attributed to the addition of AP. Adding AP into the precursor solution increases the conductivity of the solution

TGA analysis of the Al/PVDF showed two distinct events where mass was lost at approximately 190 °C and 340 °C. PVDF, in comparison, has one mass loss event occurring at approximately 500 °C as seen in Figure 4. Figure 4 (A) depicts the TGA curves at different mass loadings of n-Al in PVDF. The addition of n-Al promotes the decomposition of the polymer, despite the fact that this occurs well below the aluminum melting point. This decrease in temperature is attributed to the melting of the polymer enabling the reaction of fluorine with the alumina shell of the n-Al. This accelerates the decomposition of polymer.²⁰ Mass spectra was taken directly from the TGA and select m/z intensities were overlaid onto the TGA curve as seen in Figure 4.

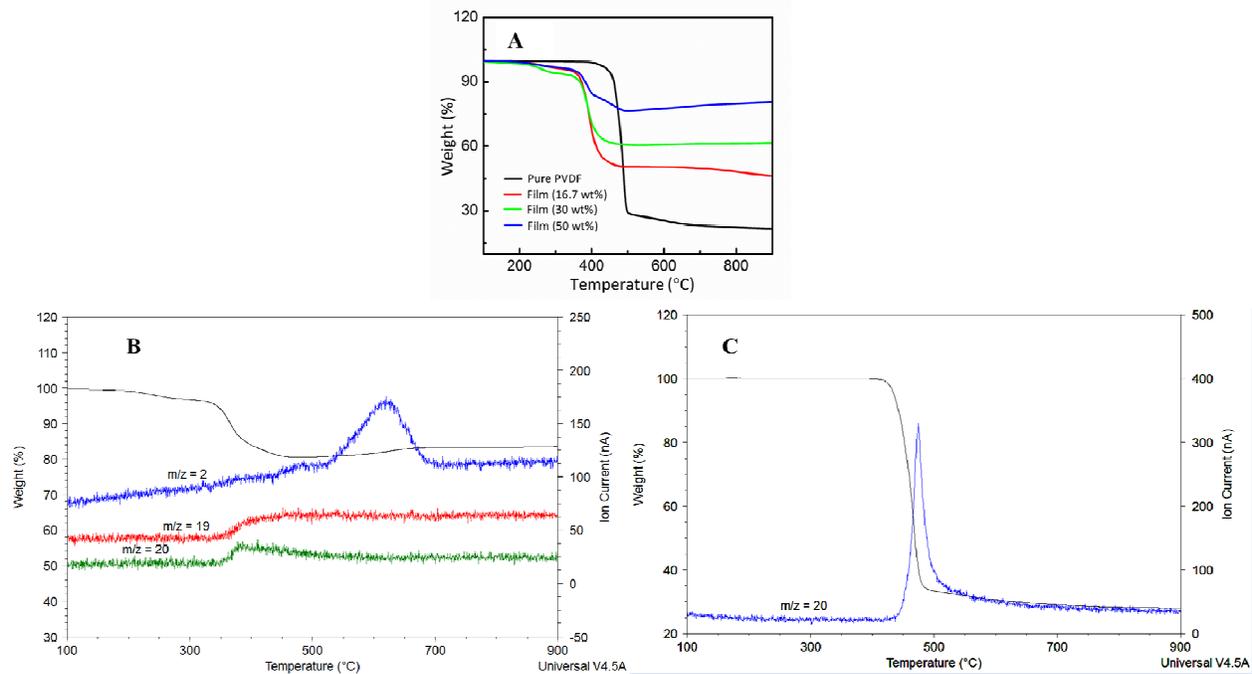


Figure 4. TGA curves of Al/PVDF with H_2O^+ , OH^+ , and H_2^+ mass spectrum intensities (A) and F^+ and HF^+ mass spectrum intensities (B). TGA curve with overlaid mass spectrum intensities for PVDF (C)

The first mass loss event is explained as the pre-ignition reaction, which has been observed previously for the reaction of n-Al and PTFE.²¹ The m/z peaks at 2, 19, and 20 correspond to H_2^+ , F^+ , and HF^+ species. These species are all also observed in the T-jump TOFMS experiments, as will be discussed later on. The relatively low signal intensity of F^+ and HF^+ is likely a result of the slow heating rates of the TGA in comparison to that of the T-jump TOFMS.

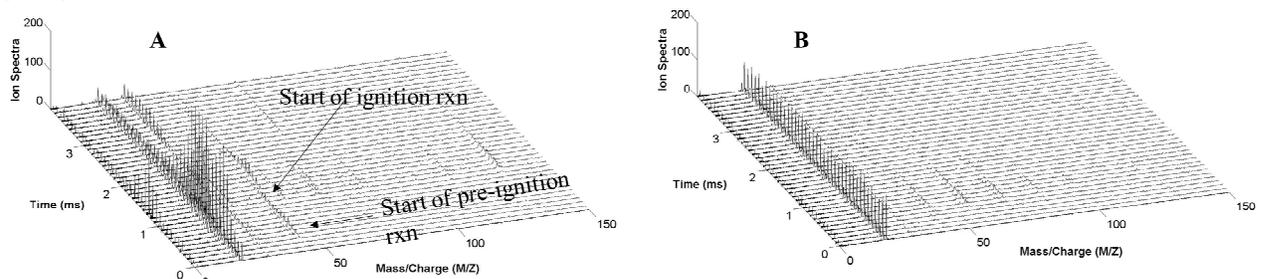


Figure 5. 3D plot of time resolved spectra for Al/PVDF (A) and PVDF (B).

The T-jump TOFMS spectra clearly show the evolution of species during the course of this reaction. The 3D plots in Figure 5 compare the reaction of Al/PVDF to the pyrolysis of pure PVDF and also show the two stages, pre-ignition and ignition, that occur during the Al/PVDF reaction. Time resolved mass spectra can be seen below for the pre-ignition and ignition events. The two separate events are labeled in the figure below. Although m/z values up to 400 were sampled, no peaks existed beyond $m/z = 150$.

At 1.7 ms, Al^+ and AlF^+ species begin to be detected. This corresponds to the beginning of the ignition reaction. As seen in the below spectra and the TGA/MS data, H_2^+ , F^+ , and HF^+ are all observed. These species have much higher relative signal intensities due to their rapid release caused by the high heating rates of the T-jump TOFMS system.

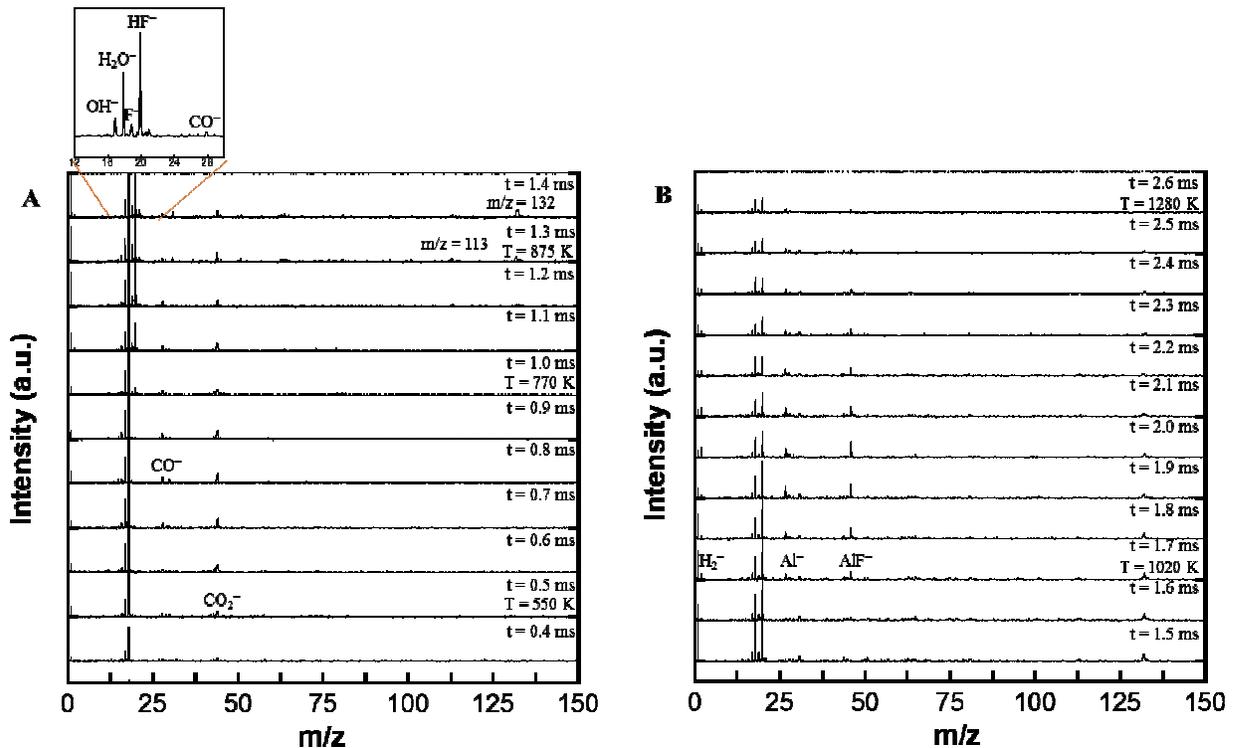


Figure 6. T-Jump TOFMS spectra of Al/PVDF during pre-ignition (A) and ignition (B) reactions.

There is a difference of $m/z = 19$ between the $m/z = 113$ and 132 peaks that become apparent at 1.3 ms, corresponding to a wire temperature of 875 K and is the loss of a F^+ due to fragmentation. The decomposition of PVDF can be seen at 0.5 ms with the appearance of CO^+ and CO_2^+ peaks. The CO^+ species at $m/z = 28$ may in actuality be C_2H_2^+ generated from fragmentation of various larger species produced during this reaction. The TOFMS spectra for the pyrolysis of pure PVDF in Figure 7 shows 4 distinct fragments with m/z values of 43, 57, 71, and 85. Each of these major peaks are spaced with a $\Delta m/z$ value of 14, corresponding to a CH_2^+ . These peaks are all also very broad representing the loss or gain of H^+ on each of these fragments.

A very small HF^+ peak is visible in the pure PVDF spectra in comparison to that of the Al/PVDF film. This peak also comes about at a much lower temperature of approximately 770 K for Al/PVDF as apposed to 890 K for the pure PVDF supporting our hypothesis that the addition of the n-Al accelerates the decomposition of the fluoropolymer.

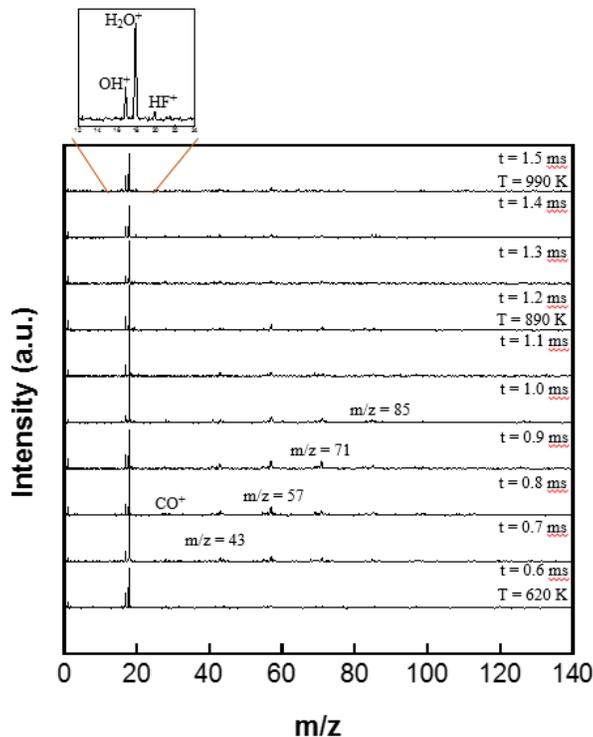
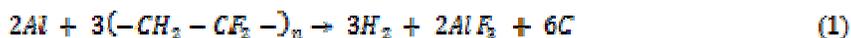
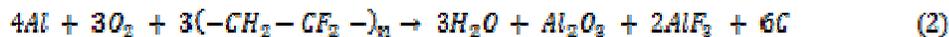


Figure 7. T-Jump TOFMS spectra of PVDF.

As reported by Zulfiqar et. al., the main decomposition product of PVDF is hydrogen fluoride (HF).²² This claim is supported by the extremely high signal intensity at $m/z = 20$ in the TOFMS spectra above. It is postulated that the Al/PVDF film reaction is as follows:



In the presence of oxygen, the burning of Al/PVDF is much more vigorous. The proposed formula for this reaction is as follows:



A series of experiments was performed on the Al/PVDF film after being electrospayed onto a platinum wire. The pressure was varied and ignition temperatures were measured for air and argon atmospheres as seen in the Figure 8. The plotted ignition temperatures show a significant decrease when pressure is increased in both air and argon atmospheres.

This trend can explain why very little visible ignition is seen during rapid heating in vacuum. The low pressure may be increasing the ignition temperature above the maximum temperature of the heated wire. The pressure within the mass spectrometer is approximately 10^{-6} torr, which is much lower than 1 atmosphere (the lowest pressure tested in the ignition temperature experiment). It is also observed in the figure above that the Al/PVDF film has an ignition temperature of approximately 50 K lower in air than argon at 1 atm. This can be attributed to the reaction between the n-Al and oxygen in the air.

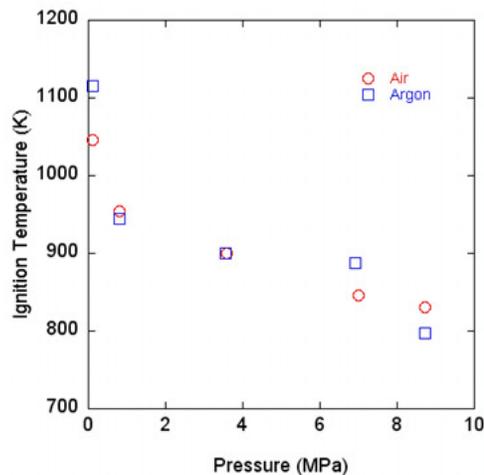


Figure 8. Ignition temperature vs pressure for Al/PVDF film electrospayed onto a platinum wire in air and argon.

IV. Conclusion

Al/PVDF free-standing films were fabricated by electrospray deposition at high particle mass loadings and homogeneous dispersion of n-Al within a PVDF matrix. Small amounts of AP were used to increase homogeneity by decreasing droplet size during the electrospray deposition process. Combustion characteristics were analyzed using TGA/MS and T-jump TOFMS. Both techniques produced results that correlated to each other and also previous work done on the PVDF fluoropolymer.

Although only very minor visible combustion is detected when heated inside the mass spectrometer, it is certain that some reaction is proceeding between the n-Al and PVDF when heated in vacuum due to the presence of the AlF^+ peak in the mass spectra above. In future studies, the TOFMS results in vacuum will be compared to the TOFMS data from ignition in air at 1 atm. The reaction mechanism in air can be further postulated by the presence of any Al_2O_3^+ signal in the spectra.

Acknowledgments

This work was financially supported by the Army Research Office (Dr. Ralph Anthenien) and a MURI grant (Dr. Mitat Birkan). We acknowledge the support of the Maryland Nanocenter and its NispLab. The NispLab is supported in part by the NSF as a MRSEC Shared Experimental Facility.

References

- ¹ Diaz, E., "Polymer Nanocomposites from energetic Thermoplastic elastomers and Alex," *Propellants, Explos. Pyrotech.*, Vol. 28, 2003, pp. 210-215.
- ² Deuskar, V. D., Mulage, K. S., Mishra, A. K., Patkar, R. N., Kharat, S. H., Kakade, S. D., "A novel hybrid binder system for extrudable composite propellant," *International Journal of Energetic Materials and Chemical Propulsion*, Vol. 11, No. 3, 2012, pp. 209-220.
- ³ Lide, D.R. *CRC Handbook of Chemistry and Physics, 77th ed*; CRC Press: Boca Raton, Florida, 1996.
- ⁴ Crouse, C. A., "Fluorinated polymers as oxidizers for energetic composites," *ACS Symposium Series: Advances in Fluorine-Containing Polymers*, Vol. 1106, Chapter 9, pp. 127-140.
- ⁵ Koch, E. C., "Metal-fluorocarbon-pyrolants: III. Development and Application of Magnesium/Teflon/Viton (MTV)," *Propellants, Explos. Pyrotech.*, Vol. 27, No. 5, 2002, pp. 262-266.
- ⁶ Wang, Y., Travas-Sejdic, J., Steiner, R., "Polymer gel electrolyte supported with microporous polyolefin membranes for lithium ion polymer battery," *Solid State Ionics* Vol. 148, No. 3-4, pp. 443-449.
- ⁷ Koch, E. C. *Metal-Fluorocarbon Based Energetic Materials*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2012.
- ⁸ Miller, H. A., Kusel, B. S., Danilson, S. T., Neat, J. W., Avjian, E. K., Pierson, S. N., Budy, S. M., Ball, D. W., Iacono, S. T., Kettwich, S. C., "Metastable nanostructured metalized fluoropolymer composites for energetics," *J. Mater. Chem. A*, Vol. 1, No. 24, 2013, pp. 7050-7058.
- ⁹ Yan, S., Jian, G. Q., Zachariah, M. R., "Electrospun NanoFiber Based Thermite Textiles and their Reaction Properties," *ACS App. Mater. Interfaces*, Vol. 4, No. 12, 2012, pp. 6432-6435.
- ¹⁰ Austin, R. A., McDowell, D. L., Benson, D. J., "Numerical simulation of shock wave propagation in spatially-resolved particle systems," *Modelling Simul. Mater. Sci. Eng.*, Vol. 14, No. 4, 2006, pp. 537-561.
- ¹¹ Bouma, R. H. B., Meuken, D., Verbeek, R., Pacheco, M. M., Katgerman, L., "Shear initiation of Al/MoO-based reactive materials," Vol. 32, No. 6, 2007, pp. 447-453.
- ¹² Meda, L., Marra, G., Galfetti, L., Inchingalo, S., Severini, F., Luca, L. D., "Nano-composites for rocket solid propellants," *Compos. Sci. Technol.*, Vol. 65, No. 5, 2005, pp. 769-773.
- ¹³ Galfetti, L., Luca, L. T. D., Severini, F., Meda, L., Marra, G., Marchetti, M., Regi, M., Bellucci, S., "Nanoparticles for solid rocket propulsion," *J. Phys. Condens. Matter*, Vol. 18, No. 33, 2006, pp. S1991-S2005.
- ¹⁴ Kim, J. H., Nam, K. W., Ma, S. B., Kim, K. B., "Fabrication and electrochemical properties of carbon nanotube film electrodes," *Carbon*, Vol. 44, No. 10, 2006, pp. 1963-1968.
- ¹⁵ Jaworek, A., "Electrospray droplet sources for thin film deposition," *J. Mater. Sci.*, Vol. 42, No. 1, 2007, pp. 266-297.
- ¹⁶ Rietveld, I. B., Suganuma, N., Kobayashi, K., Yamada, H., Matsushige, K., "Electrospray deposition of photoresist: a low impact method for the fabrication of multilayered films," *Macromol. Mater. Eng.*, Vol. 293, No. 5, 2008, pp. 387-399.
- ¹⁷ Zhou, L., Piekielek, N., Chowdhury, S., Zachariah, M. R., "T-jump/time of flight mass spectrometry for time resolved analysis of fast condensed state reactions," *47th AIAA Aerospace Sciences Meeting Including The New Horizons Forum and Aerospace Exposition*, 5 - 8 January, Orlando, Florida, 2009.
- ¹⁸ Zhou, L., Piekielek, N., Chowdhury, S., Zachariah, M. R., "T-Jump/time-of-flight mass spectrometry for time-resolved analysis of energetic materials," *Rapid Commun. Mass Spectrom.*, Vol. 23, No. 1, 2009, pp. 194-202.
- ¹⁹ Rietveld, I. B., Kobayashi, K., Yamada, H., Matsushige, K., "Process parameters for fast production of ultra-thin polymer film with electrospray deposition under ambient conditions," *J. Colloid Interface Sci.*, Vol. 339, No. 2, 2009, pp. 481-488.
- ²⁰ Pantoya, M. L., Dean, S. W., "The influence of alumina passivation on nano-Al/Teflon reactions," *Thermochim. Acta*, Vol. 493, No. 1-2, 2009, pp. 109-110.

²¹ Osborne, D. T., Pantoya, M. L., "Effect of Al particle size on the thermal degradation of Al/Teflon mixtures," *Combust. Sci. and Tech.*, Vol. 179, No. 8, 2007, pp. 1467-1480.

²² Zulfiqar, S., Zulfiqar, M., Rizvi, M., Munir, A., "Study of the thermal degradation of PCTFE, PVDF, and copolymers of CTFE and VDF," *Polym. Degrad. Stab.*, Vol. 43, No. 3, 1994, pp. 423-430.