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**More than Piezoelectricity: Harnessing Electroactive Materials for Functional Energetics**

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<b>14. ABSTRACT</b> Over the course of the last few years there has been an increased interest in exploring energetics that have exhibit electroactive properties. Indeed, they offer the hope for reactive materials, from propellants to explosives, to be multifunctional and capable of control via external stimuli (smart materials). In early work by the Son group the terpolymer, tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride, in combination with nanoscale aluminum, demonstrated unique behavior that was attributed to its piezoelectricity. To fully harness these effects, one must understand their role in providing control to energetic materials. In this first year we have made significant progress in several areas of this research: 1) Understanding the flexoelectric effect for PVDF and THV; 2) initial synthesis of PVDF coated aluminum particles; and 3) synthesis of perovskite energetic crystals.			
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**More than Piezoelectricity: Harnessing Electroactive Materials for Functional Energetics  
YEAR 3 REPORT**

**FA9550-19-1-0289**

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Undergraduate Students: Jake Martinelli/Jay Horning

## Abstract

In the past few years, there has been an increased interest in exploring energetics that exhibit electroactive properties. Indeed, they offer the hope for reactive materials, from propellants to explosives, to be multifunctional and capable of control via external stimuli (smart materials). This work is specifically focused on exploring these reactive materials and developing new materials that can be controlled. In year one we made significant progress in several areas of this research: 1) understanding the flexoelectric effect for PVDF and THV; 2) initial synthesis of PVDF coated aluminum particles, and 3) synthesis of perovskite energetic crystals. In year two, we continued detailed studies with these materials, explored an additional fuel material, magnesium diboride ( $\text{MgB}_2$ ), and prepared to publish the Al-fluoropolymer measurements. In year **three**, we continued our work in the following areas: 1) determination of flexo and piezoelectric coefficients for the THV- $\text{MgB}_2$  reactive system, 2) Synthesis of beta-phase nano PVDF particles for inclusion in reactive formulations, 3) composite propellant formulations with HTPB- $\text{MgB}_2$ -AP and associated measurements, 4) continued synthesis of molecular perovskites and propellant formulations with such, and 5) we collaborated with Min Zhou and his student at Georgia Tech to complete modeling of the flexoelectric response of THV-Al reactive systems. This project is under a NCE and we anticipate completing critical tasks but may require an additional NCE period due to lack of graduate student availability.

## Background

Piezoelectricity is defined as electric polarization in a substance resulting from the application of mechanical stress. Therefore, one might consider that when we stress an energetic formulation appropriately an electrical charge will be generated or the converse. That electrical charge might be sufficient to alter the ignition threshold or overall sensitivity of the material. The flexoelectric effect is when a dielectric material exhibits a spontaneous electrical polarization induced by a strain gradient. Therefore, straining can induce electrical polarization and potentially alter the ignition characteristics. While the fluoropolymer-nanoaluminum system has demonstrated that functional energetics could potentially be achieved it cannot serve as a standalone formulation for propulsion. Therefore, there is an outstanding need to develop *new* energetic materials that can adequately serve propulsion needs and be designed into smart materials. ***This report details the progress towards this for the third year of this project.*** To accomplish the goals of this proposal there are three primary thrusts that include i) synthesis and fabrication, ii) material characterization, and iii) performance characterization. In the third year we have focused on additional material characterization and specific synthesis and fabrication. Each area and the results obtained thus far are detailed below.

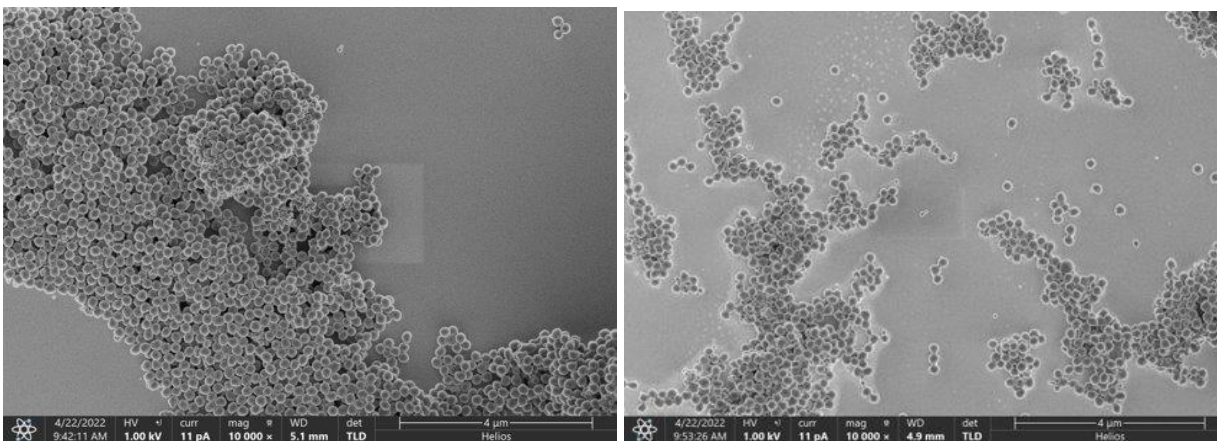
## Results (YR3)

A primary focus of this third year was to push our THV-Al publication out the door, collaborate with Georgia Tech on modeling of flexoelectricity, and fabricate and characterize composite materials with down selected inclusions. This report is broken into the key results from each of these focal areas and detailed below. In year two, we had begun exploration of  $\text{MgB}_2$  as an alternative fuel for these flexoelectric reactive materials and we spent a significant amount of time focused on two material systems containing  $\text{MgB}_2$ . The first, is continuation work of reactive and dielectric characteristics of  $\text{MgB}_2$ /THV and the second, is the exploration of  $\text{MgB}_2$  in composite propellant formulations. There is no literature on  $\text{MgB}_2$  as a propellant additive to date. We also

spent and continue to spend time exploring the synthesis of nanoscale PVDF so that we may add it as an inclusion material into our composite formulations. Those results are presently being further detailed and a short communication on the precipitation process was submitted to Materials Letters. This represents an entirely new way of synthesizing beta phase PVDF particles with size/morphology control.

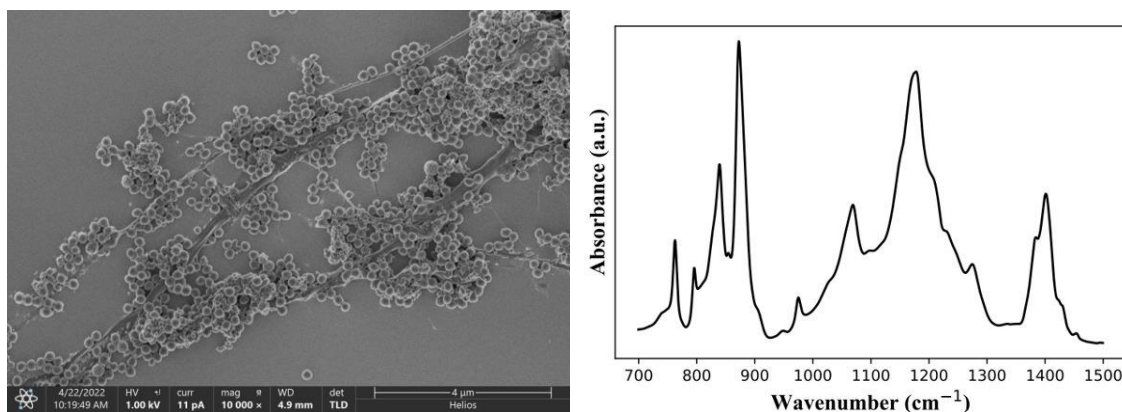
### Nano PVDF (nPVDf)

Continued work on crash precipitation of nano-PVDF has indicated that we can synthesize particles that have a reasonably high fraction of the beta phase, and this represents a simple route for the synthesis of inclusions that can enhance the electroactive response of energetic materials as well as many other composite systems.



**Figure 1.** nPVDF particles synthesized via the simple crash precipitation route, Left (1/20 ratio) and Right (1/30 ratio)- PVDF/DMF.

At this point, we have synthesized particles for varying PVDF/DMF ratio, temperature, rate of addition, and HF quantity. The results indicate that by varying the ratio of PVDF/DMF that the beta fraction is increased – particle size is nominally around 200 nm as indicated by the images shown in Figure 1. With an increase in DMF we see the appearance of more fibril structures such as that shown in Figure 2.



**Figure 2.** (Left) nPVDF particles synthesized at a ratio of 1g PVDF/60 ml DMF and (Right) FTIR indicating beta phase (~60%).

With temperature we still see distinct particles form but the phase is predominately in the alpha phase indicating that temperature needs to be closely controlled to ensure the maximum beta fraction is achieved. The role of HF in achieving beta fraction PVDF is also critical – it appears with excess HF that the beta fraction goes down – we have not fully elucidated this mechanistically. Particle imaging still needs to be conducted to determine the morphology of the particulates as the initial appearance is globular.

The materials with the highest beta phase will be used for formulating composite formulations for flexo and piezo measurements. Our present target is boron formulations to build upon our previous flexoelectric measurements with this system and would allow for unique reactive propulsion systems (like B/PTFE) to be formulated that have the potential to behave as piezoelectrics/flexoelectrics.

**MgB<sub>2</sub> in HTPB/AP composite propellant.**

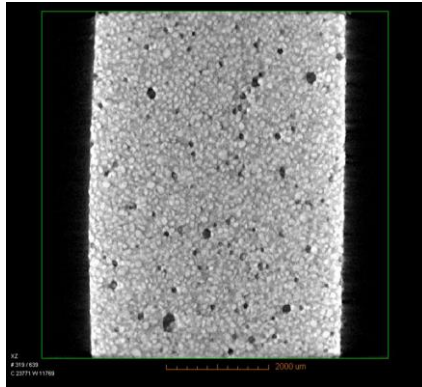
Several previous studies, including our own, have indicated that MgB<sub>2</sub> could serve as an excellent fuel in combination with fluoropolymers (oxidizer) but there is no work in the literature detailing MgB<sub>2</sub> as an efficient fuel/catalyst in composite propellant. Based on our year 2 results that indicate that MgB<sub>2</sub> ALSO acts as a true piezoelectric we selected to formulate an HTPB/AP composite propellant and detail the resulting flexoelectric response. We are also preparing those samples for burning rate analysis with the addition of MgB<sub>2</sub>. As summarized in Table 1 the transverse flexoelectric response is relatively high for HTPB/AP samples and the inclusion of MgB<sub>2</sub> does not significantly enhance nor decrease this. It should be noted that these values are higher than the Al/THV reactive system and indicate that with significant non-uniform strain applied that we would expect hot spots to form for the material. We hope in year 4, during the NCE, that we can continue collaborations with Min Zhou to elucidate if dielectric breakdown will occur for these samples as well and potentially lead to thermal events. To compare, we may also consider what the apparent piezoelectric coefficient is for these materials. *In order to do so mechanical testing of these samples was conducted and a low elastic modulus of ~ 5 MPa was observed (typical of composite propellant) and when we use that number to calculate the apparent piezoelectric coefficient, d<sub>33</sub>, a value of ~2000 pC/N is calculated. This is higher than PZT and represents the first time the materials community would consider HTPB bound materials for responsive materials. In fact, even if a conservative value is taken to account for experimental error the apparent piezoelectric coefficient is considered to be giant.*

**Table 1.** Transverse Flexoelectric coefficient for HTPB bound samples with and without AP/MgB<sub>2</sub> inclusions.

<b>Material</b>	<b>Transverse Flexoelectric Coefficient (nC/m)</b>
HTPB nonporous	5.0 +/- 0.6
HTPB porous	6.8 +/- 0.7
HTPB/AP 80 wt% solids	14.5 +/- 1.9

HTPB/AP/MgB <sub>2</sub> (20/75/5 wt%)	11.9+/- 1.3
HTPB/AP/MgB <sub>2</sub> (20/70/10 wt%)	12.2 +/- 0.1
HTPB/AP/MgB <sub>2</sub> (20/65/15 wt%)	11.4 +/- 0.4

We have conducted microCT on the host of samples and have observed what we would consider excessive porosity (Figure 3) for burning rate measurements (at pressure) and therefore we are in the process of remaking these samples and sending them to our collaborators for analysis. These samples will be sent to Travis Sippel to conduct pressurized burning rate measurements. We have done atmospheric burning rates of these materials and the nominal burning rates are on the order of 3 mm/s regardless of MgB<sub>2</sub> loading. Upon ignition, there is clear indication of green light emitting products (BO<sub>2</sub> and other) indicating combustion of MgB<sub>2</sub>.



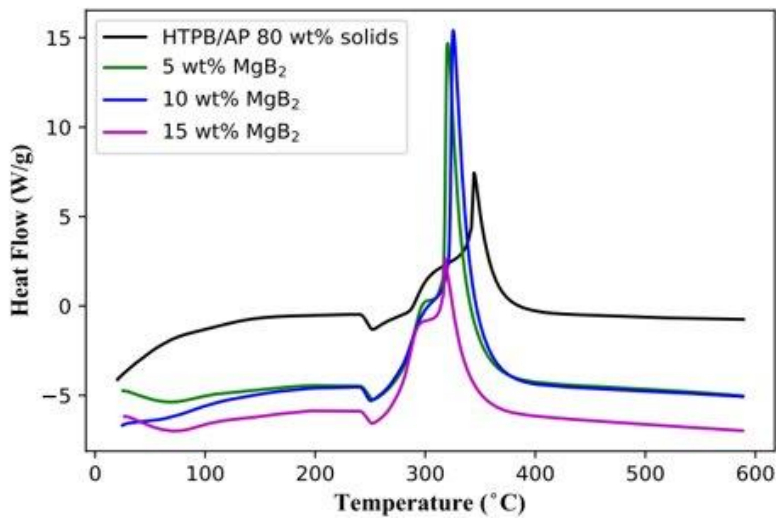
**Figure 3.** Micro CT of HTPB/AP/MgB<sub>2</sub> composite (20/65/15) showing the pores within the sample.



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Thermal analysis of these formulations via DSC indicates that MgB<sub>2</sub> acts as a catalyst for the decomposition of ammonium perchlorate as there is a clear shift in the onset of reaction and an

increase in the peak energy output as shown in Figure 5. We are presently completing studies with just ammonium perchlorate and  $\text{MgB}_2$  so that we can assess catalytic effects.



**Figure 5.** DSC heatflow data for HTPB/AP/ $\text{MgB}_2$  loaded composite propellant.

#### Major findings for YR 3 include:

- Reactive composites of THV/ $\text{MgB}_2$  exhibit strong flexoelectric behavior and are demonstrated to be responsive in nature (true “smart” material).
- Nanosized PVDF acts as a polarizable inclusion material and can significantly enhance the flexoelectric effect in composite reactive structures. The synthesis route/method results in high beta-phase material and represents a unique method for achieving nanosized electroactive inclusions.
- $\text{MgB}_2$  is found to be an exceptional inclusion material in composite propellant formulations and acts as a fuel as well as a catalyst for the decomposition of ammonium perchlorate.

**Presentations:** This year we plan on presenting at both the GRC Energetic Materials and the International Pyrotechnics Symposium.

1. “Flexoelectricity in Reactive Systems”, **M.J. Zaitzeff\*** and L.J. Groven, Proceedings of the 45<sup>th</sup> International Pyrotechnics Symposium, Colorado Springs, CO, July 10-15<sup>th</sup>, 2022.
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#### Papers:

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4. Shin, J, Zaitzeff, M.J., Groven, L.J., Zhou, M., Microstructure Enhancement of Macroscopic Flexoelectric Behavior of THV/Al Composites, *J. Appl Phys.*, in preparation.

**Personnel funded:** One full time PhD student, Mikel Zaitzeff, and one full time MS student funded from this effort. Summer salary for PI. Part time undergraduate support during summer.

**Year 4+ (NCE year +) Efforts:**

The primary goal for our year four efforts will be focused on completing detailed studies of MgB<sub>2</sub>, Boron, and crystal inclusions. We will also downselect a composite system for demonstrating as a smart reactive.

Research Thrusts and Tasks	Year 1				Year 2				Year 3				Year 4 +
	1	2	3	4	1	2	3	4	1	2	3	4	
<b>Synthesis &amp; Fabrication</b>													
Milled fluoropolymer/fuel particles													
Fluoropolymer coated fuel particles													
Polymer coated burning rate enhancers													
Polymer coated crystals and composite structures													
Synthesis of energetic perovskites													
Fabrication of composites with downselected inclusions													
FDM of fluoropolymer for enhanced piezoactive phase													
<b>Material Characterization</b>													
Structure & Morphology													
Reactivity, thermal characteristics													
Dielectric properties													
Piezoelectric properties													
Flexoelectric properties													
<b>Performance Characterization</b>													
Design of relevant experiment from Thrust 2													
Field Activated Combustion													
Localized Ignition of Functionally Graded Materials													

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## Abstract

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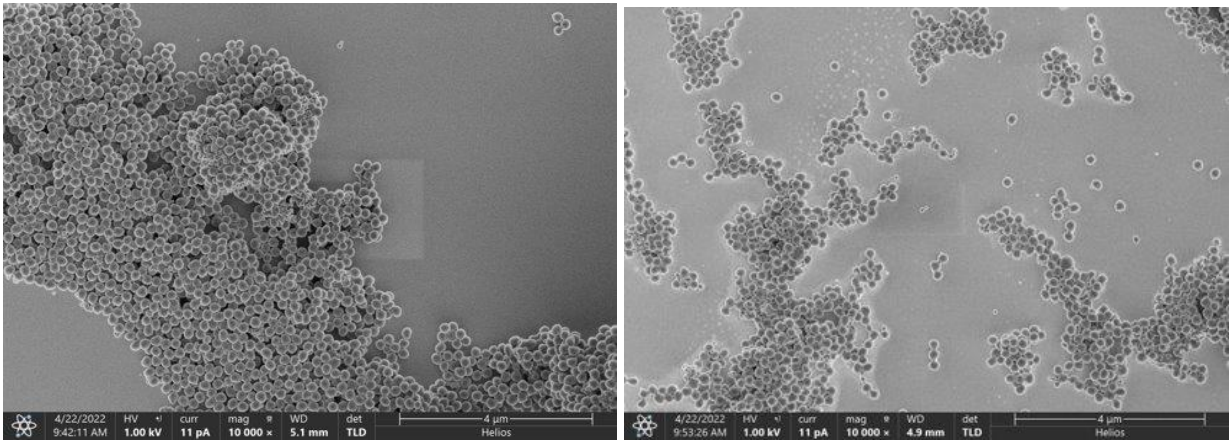
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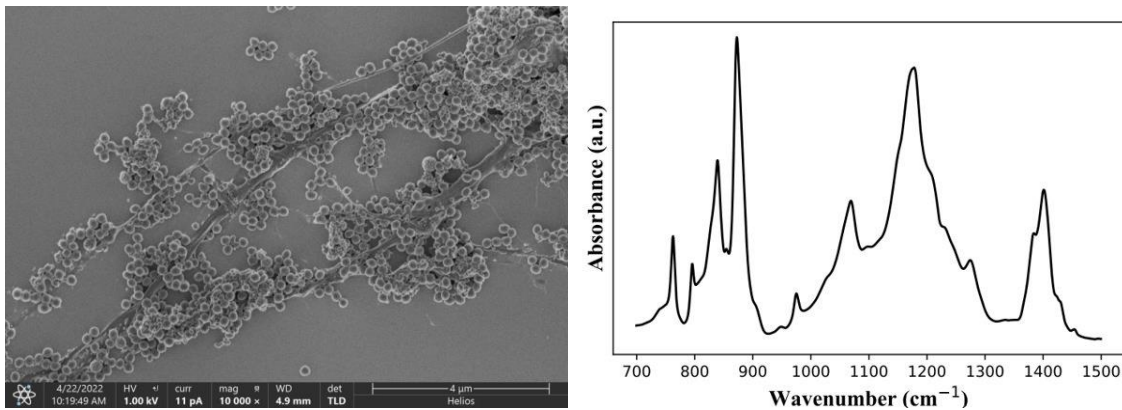
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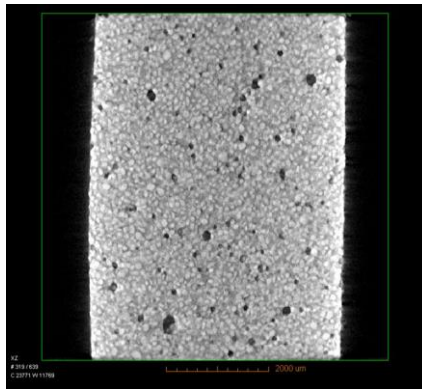
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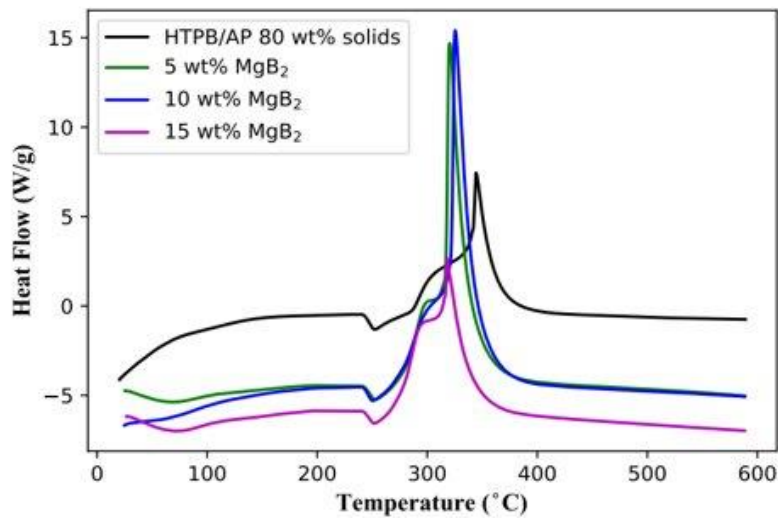
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Research Thrusts and Tasks	Year 1				Year 2				Year 3				Year 4 +
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<b>Synthesis &amp; Fabrication</b>													
Milled fluoropolymer/fuel particles													
Fluoropolymer coated fuel particles													
Polymer coated burning rate enhancers													
Polymer coated crystals and composite structures													
Synthesis of energetic perovskites													
Fabrication of composites with downselected inclusions													
FDM of fluoropolymer for enhanced piezoactive phase													
<b>Material Characterization</b>													
Structure & Morphology													
Reactivity, thermal characteristics													
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<b>Performance Characterization</b>													
Design of relevant experiment from Thrust 2													
Field Activated Combustion													
Localized Ignition of Functionally Graded Materials													

**More than Piezoelectricity: Harnessing Electroactive Materials for Functional Energetics  
YEAR 3 REPORT**

**FA9550-19-1-0289**

*Participants:*

Technical Point of Contact

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PhD Student: Mikel Zaitzeff

MS Student: Shakole Rugh

Undergraduate Students: Jake Martinelli/Jay Horning

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## Background

Piezoelectricity is defined as electric polarization in a substance resulting from the application of mechanical stress. Therefore, one might consider that when we stress an energetic formulation appropriately an electrical charge will be generated or the converse. That electrical charge might be sufficient to alter the ignition threshold or overall sensitivity of the material. The flexoelectric effect is when a dielectric material exhibits a spontaneous electrical polarization induced by a strain gradient. Therefore, straining can induce electrical polarization and potentially alter the ignition characteristics. While the fluoropolymer-nanoaluminum system has demonstrated that functional energetics could potentially be achieved it cannot serve as a standalone formulation for propulsion. Therefore, there is an outstanding need to develop *new* energetic materials that can adequately serve propulsion needs and be designed into smart materials. ***This report details the progress towards this for the third year of this project.*** To accomplish the goals of this proposal there are three primary thrusts that include i) synthesis and fabrication, ii) material characterization, and iii) performance characterization. In the third year we have focused on additional material characterization and specific synthesis and fabrication. Each area and the results obtained thus far are detailed below.

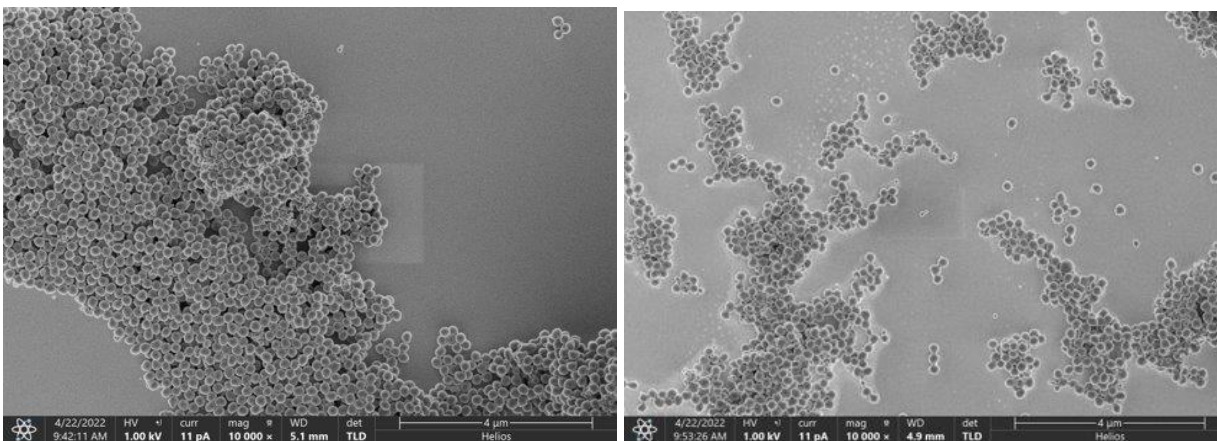
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spent and continue to spend time exploring the synthesis of nanoscale PVDF so that we may add it as an inclusion material into our composite formulations. Those results are presently being further detailed and a short communication on the precipitation process was submitted to Materials Letters. This represents an entirely new way of synthesizing beta phase PVDF particles with size/morphology control.

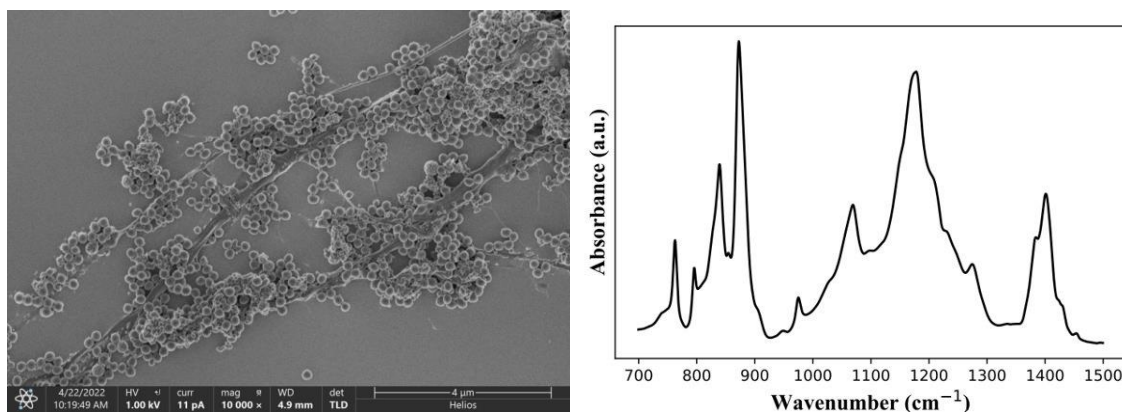
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**Figure 1.** nPVDF particles synthesized via the simple crash precipitation route, Left (1/20 ratio) and Right (1/30 ratio)- PVDF/DMF.

At this point, we have synthesized particles for varying PVDF/DMF ratio, temperature, rate of addition, and HF quantity. The results indicate that by varying the ratio of PVDF/DMF that the beta fraction is increased – particle size is nominally around 200 nm as indicated by the images shown in Figure 1. With an increase in DMF we see the appearance of more fibril structures such as that shown in Figure 2.



**Figure 2.** (Left) nPVDF particles synthesized at a ratio of 1g PVDF/60 ml DMF and (Right) FTIR indicating beta phase (~60%).

With temperature we still see distinct particles form but the phase is predominately in the alpha phase indicating that temperature needs to be closely controlled to ensure the maximum beta fraction is achieved. The role of HF in achieving beta fraction PVDF is also critical – it appears with excess HF that the beta fraction goes down – we have not fully elucidated this mechanistically. Particle imaging still needs to be conducted to determine the morphology of the particulates as the initial appearance is globular.

The materials with the highest beta phase will be used for formulating composite formulations for flexo and piezo measurements. Our present target is boron formulations to build upon our previous flexoelectric measurements with this system and would allow for unique reactive propulsion systems (like B/PTFE) to be formulated that have the potential to behave as piezoelectrics/flexoelectrics.

### **MgB<sub>2</sub> in HTPB/AP composite propellant.**

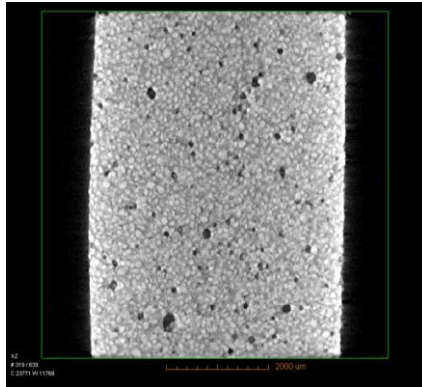
Several previous studies, including our own, have indicated that MgB<sub>2</sub> could serve as an excellent fuel in combination with fluoropolymers (oxidizer) but there is no work in the literature detailing MgB<sub>2</sub> as an efficient fuel/catalyst in composite propellant. Based on our year 2 results that indicate that MgB<sub>2</sub> ALSO acts as a true piezoelectric we selected to formulate an HTPB/AP composite propellant and detail the resulting flexoelectric response. We are also preparing those samples for burning rate analysis with the addition of MgB<sub>2</sub>. As summarized in Table 1 the transverse flexoelectric response is relatively high for HTPB/AP samples and the inclusion of MgB<sub>2</sub> does not significantly enhance nor decrease this. It should be noted that these values are higher than the Al/THV reactive system and indicate that with significant non-uniform strain applied that we would expect hot spots to form for the material. We hope in year 4, during the NCE, that we can continue collaborations with Min Zhou to elucidate if dielectric breakdown will occur for these samples as well and potentially lead to thermal events. To compare, we may also consider what the apparent piezoelectric coefficient is for these materials. *In order to do so mechanical testing of these samples was conducted and a low elastic modulus of ~ 5 MPa was observed (typical of composite propellant) and when we use that number to calculate the apparent piezoelectric coefficient,  $d_{33}$ , a value of ~2000 pC/N is calculated. This is higher than PZT and represents the first time the materials community would consider HTPB bound materials for responsive materials. In fact, even if a conservative value is taken to account for experimental error the apparent piezoelectric coefficient is considered to be giant.*

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<b>Material</b>	<b>Transverse Flexoelectric Coefficient (nC/m)</b>
HTPB nonporous	5.0 +/- 0.6
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HTPB/AP/MgB <sub>2</sub> (20/75/5 wt%)	11.9+/- 1.3
HTPB/AP/MgB <sub>2</sub> (20/70/10 wt%)	12.2 +/- 0.1
HTPB/AP/MgB <sub>2</sub> (20/65/15 wt%)	11.4 +/- 0.4

We have conducted microCT on the host of samples and have observed what we would consider excessive porosity (Figure 3) for burning rate measurements (at pressure) and therefore we are in the process of remaking these samples and sending them to our collaborators for analysis. These samples will be sent to Travis Sippel to conduct pressurized burning rate measurements. We have done atmospheric burning rates of these materials and the nominal burning rates are on the order of 3 mm/s regardless of MgB<sub>2</sub> loading. Upon ignition, there is clear indication of green light emitting products (BO<sub>2</sub> and other) indicating combustion of MgB<sub>2</sub>.



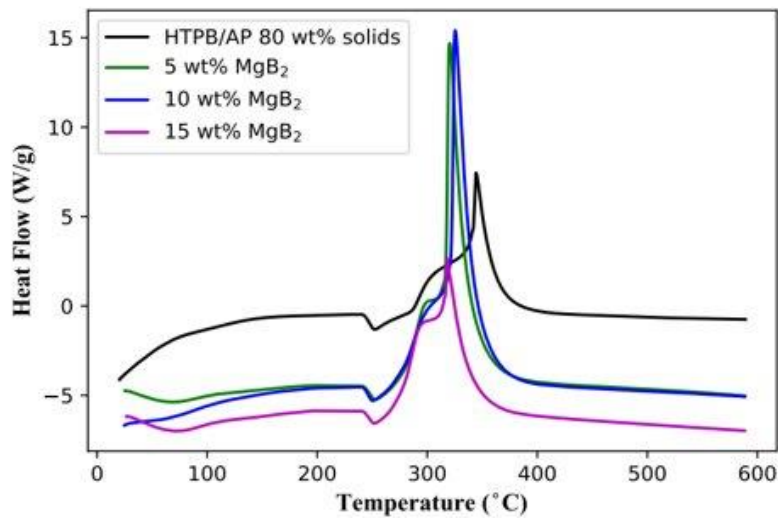
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Thermal analysis of these formulations via DSC indicates that MgB<sub>2</sub> acts as a catalyst for the decomposition of ammonium perchlorate as there is a clear shift in the onset of reaction and an

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**Figure 5.** DSC heatflow data for HTPB/AP/ $\text{MgB}_2$  loaded composite propellant.

#### Major findings for YR 3 include:

- Reactive composites of THV/ $\text{MgB}_2$  exhibit strong flexoelectric behavior and are demonstrated to be responsive in nature (true “smart” material).
- Nanosized PVDF acts as a polarizable inclusion material and can significantly enhance the flexoelectric effect in composite reactive structures. The synthesis route/method results in high beta-phase material and represents a unique method for achieving nanosized electroactive inclusions.
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**Presentations:** This year we plan on presenting at both the GRC Energetic Materials and the International Pyrotechnics Symposium.

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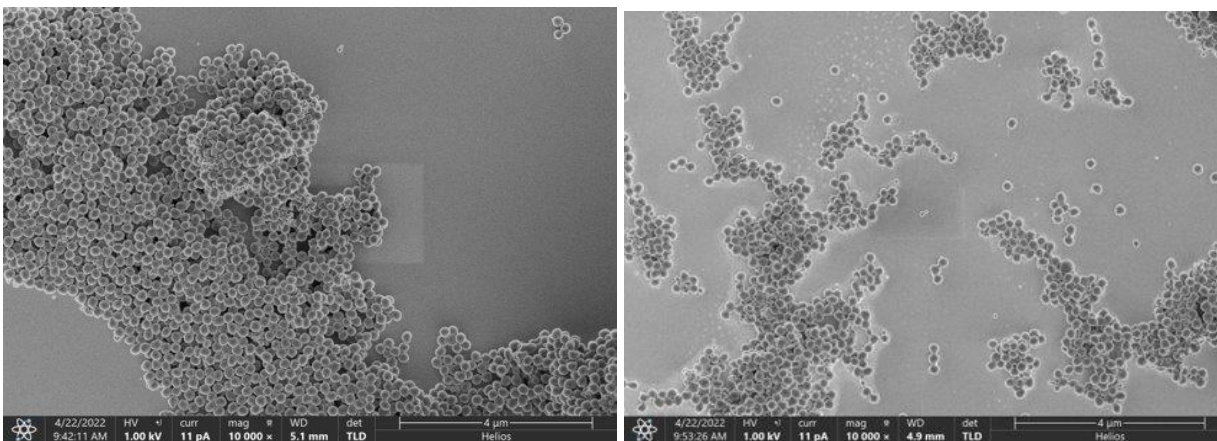
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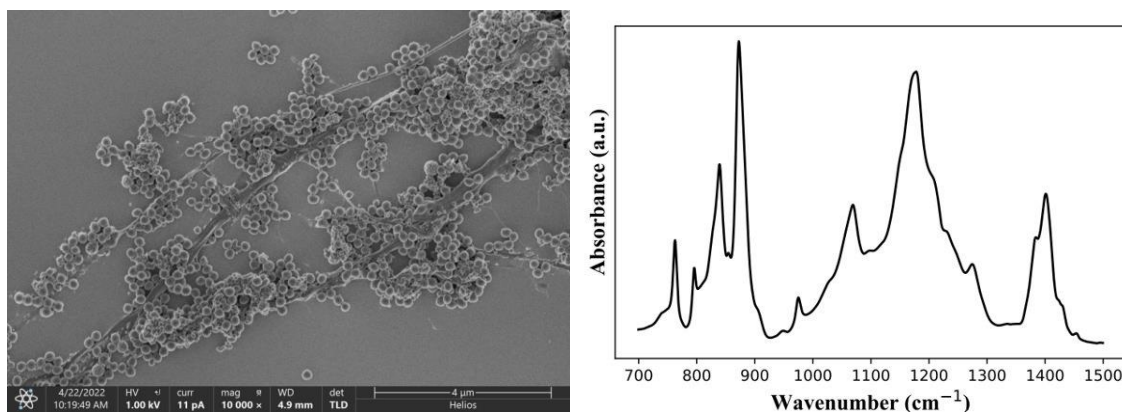
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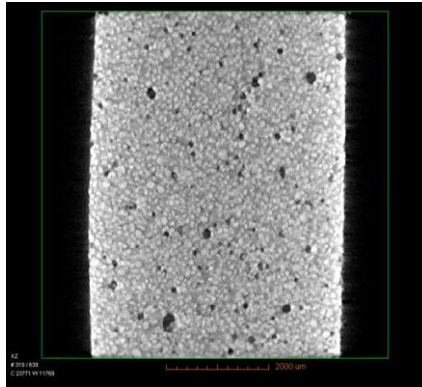
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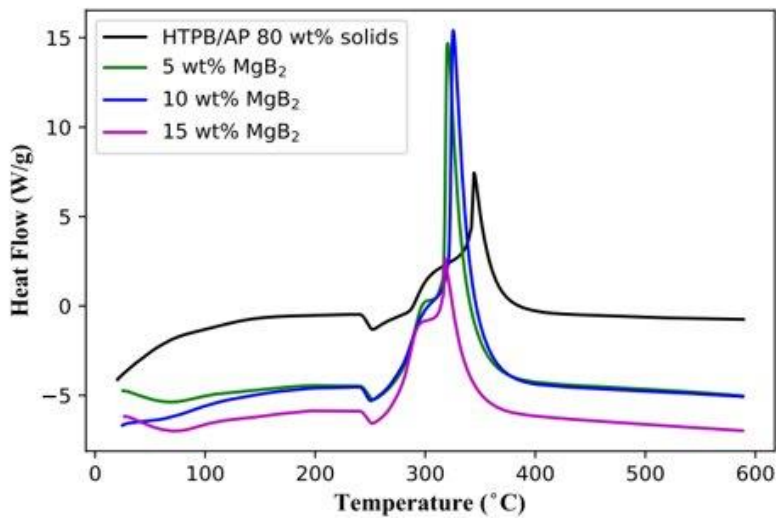
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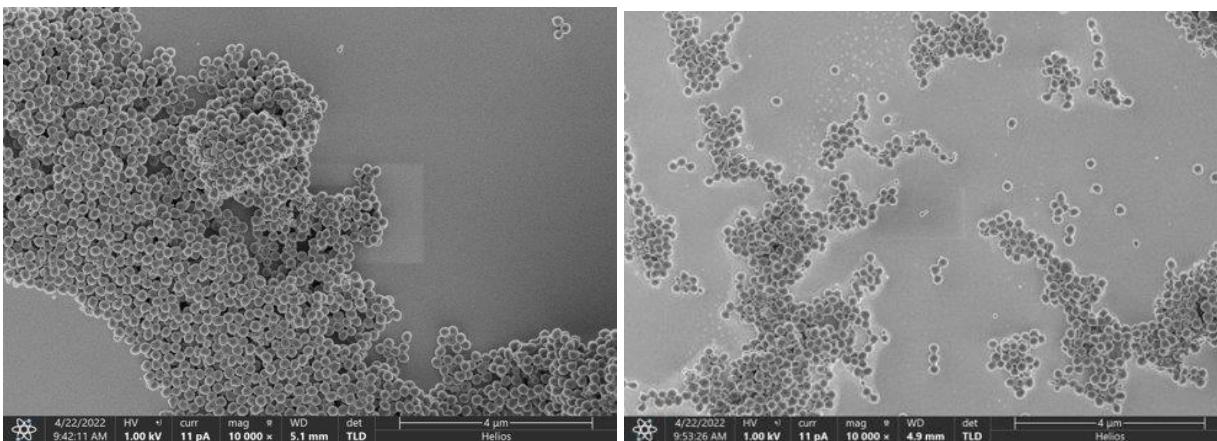
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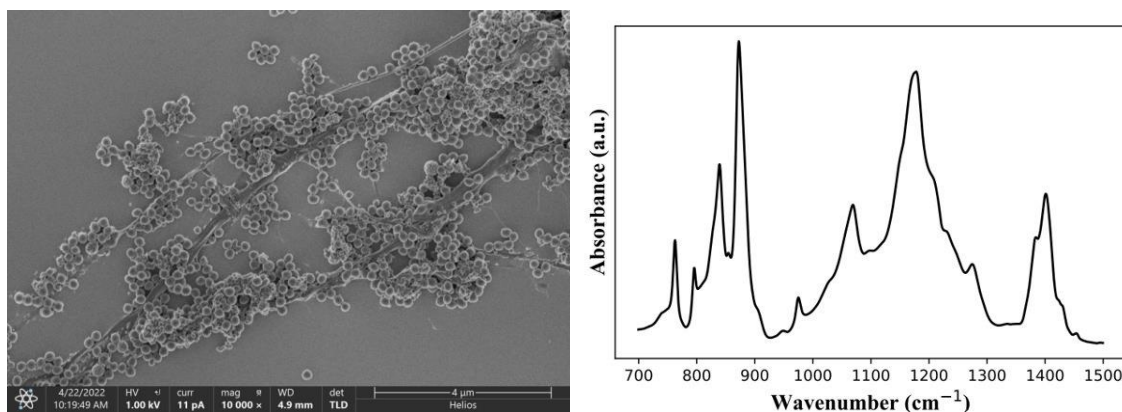
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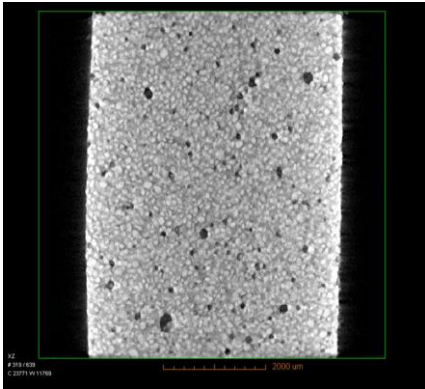
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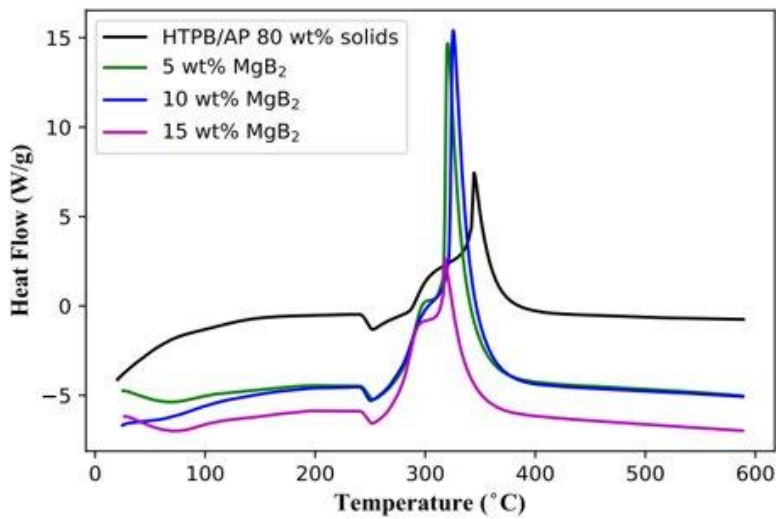
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YEAR 3 REPORT**

**FA9550-19-1-0289**

*Participants:*

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Graduate Students:

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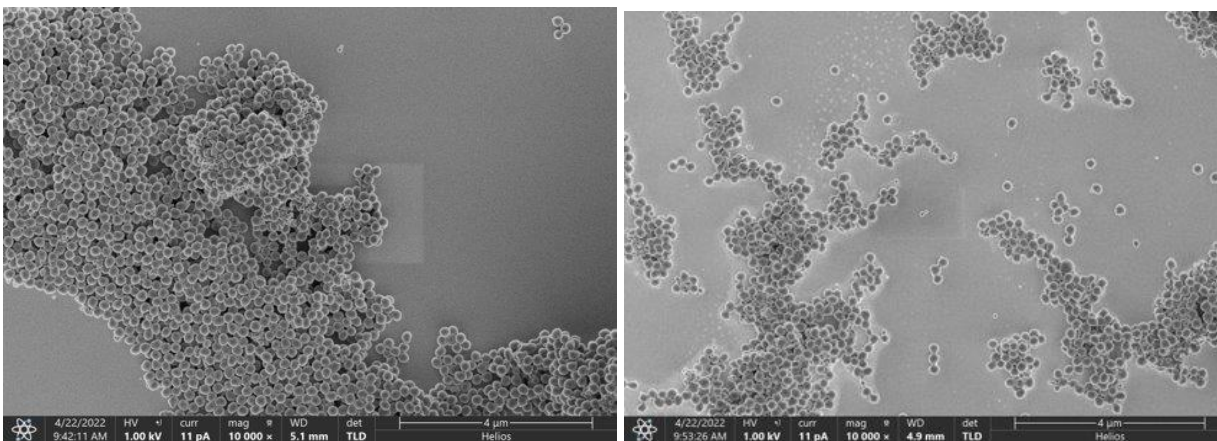
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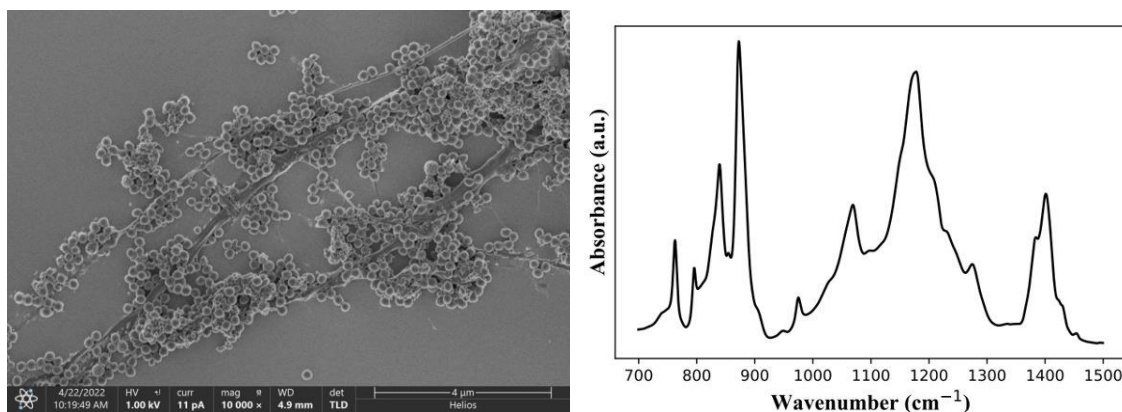
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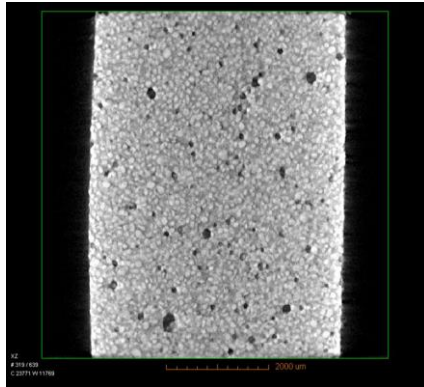
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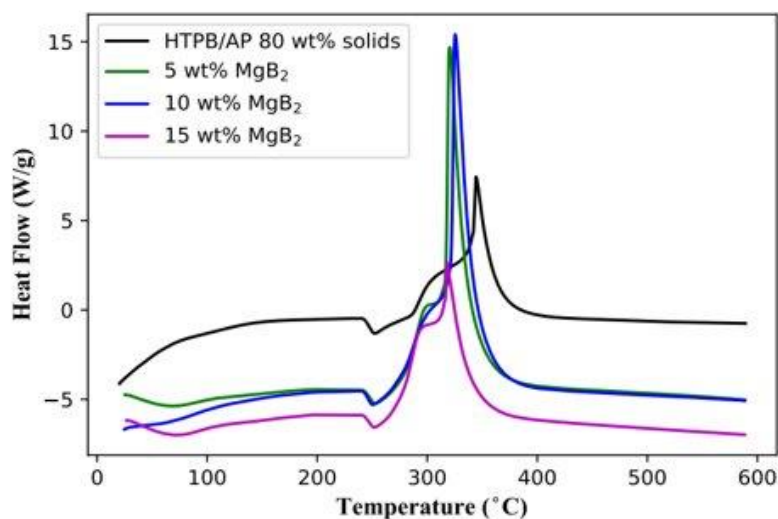
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**Personnel funded:** One full time PhD student, Mikel Zaitzeff, and one full time MS student funded from this effort. Summer salary for PI. Part time undergraduate support during summer.

**Year 4+ (NCE year +) Efforts:**

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Research Thrusts and Tasks	Year 1				Year 2				Year 3				Year 4 +
	1	2	3	4	1	2	3	4	1	2	3	4	
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Fluoropolymer coated fuel particles													
Polymer coated burning rate enhancers													
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Structure & Morphology													
Reactivity, thermal characteristics													
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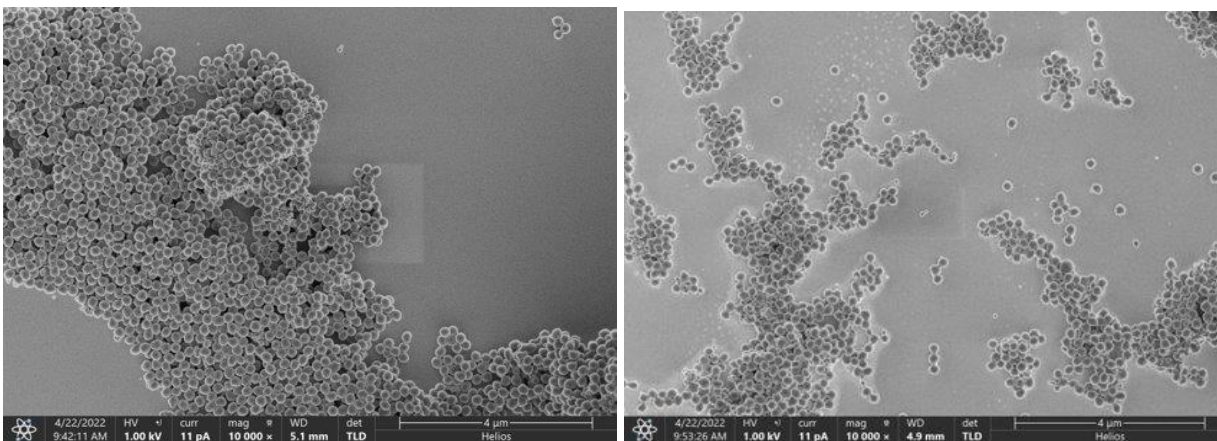
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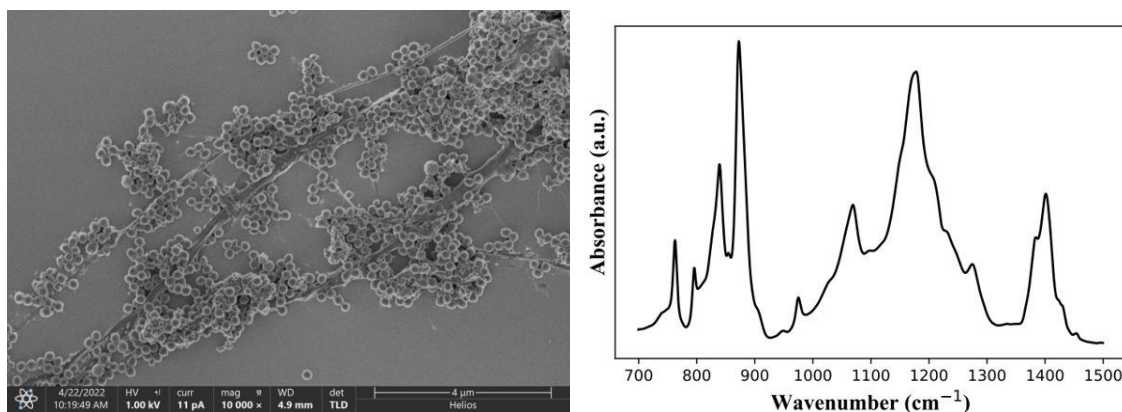
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At this point, we have synthesized particles for varying PVDF/DMF ratio, temperature, rate of addition, and HF quantity. The results indicate that by varying the ratio of PVDF/DMF that the beta fraction is increased – particle size is nominally around 200 nm as indicated by the images shown in Figure 1. With an increase in DMF we see the appearance of more fibril structures such as that shown in Figure 2.



**Figure 2.** (Left) nPVDF particles synthesized at a ratio of 1g PVDF/60 ml DMF and (Right) FTIR indicating beta phase (~60%).

With temperature we still see distinct particles form but the phase is predominately in the alpha phase indicating that temperature needs to be closely controlled to ensure the maximum beta fraction is achieved. The role of HF in achieving beta fraction PVDF is also critical – it appears with excess HF that the beta fraction goes down – we have not fully elucidated this mechanistically. Particle imaging still needs to be conducted to determine the morphology of the particulates as the initial appearance is globular.

The materials with the highest beta phase will be used for formulating composite formulations for flexo and piezo measurements. Our present target is boron formulations to build upon our previous flexoelectric measurements with this system and would allow for unique reactive propulsion systems (like B/PTFE) to be formulated that have the potential to behave as piezoelectrics/flexoelectrics.

**MgB<sub>2</sub> in HTPB/AP composite propellant.**

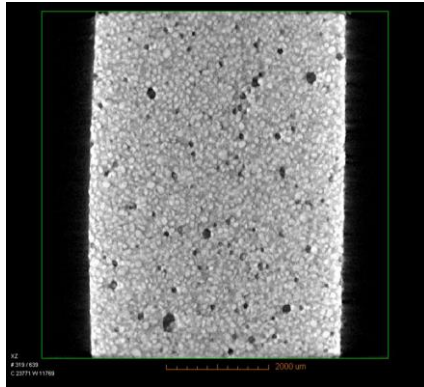
Several previous studies, including our own, have indicated that MgB<sub>2</sub> could serve as an excellent fuel in combination with fluoropolymers (oxidizer) but there is no work in the literature detailing MgB<sub>2</sub> as an efficient fuel/catalyst in composite propellant. Based on our year 2 results that indicate that MgB<sub>2</sub> ALSO acts as a true piezoelectric we selected to formulate an HTPB/AP composite propellant and detail the resulting flexoelectric response. We are also preparing those samples for burning rate analysis with the addition of MgB<sub>2</sub>. As summarized in Table 1 the transverse flexoelectric response is relatively high for HTPB/AP samples and the inclusion of MgB<sub>2</sub> does not significantly enhance nor decrease this. It should be noted that these values are higher than the Al/THV reactive system and indicate that with significant non-uniform strain applied that we would expect hot spots to form for the material. We hope in year 4, during the NCE, that we can continue collaborations with Min Zhou to elucidate if dielectric breakdown will occur for these samples as well and potentially lead to thermal events. To compare, we may also consider what the apparent piezoelectric coefficient is for these materials. *In order to do so mechanical testing of these samples was conducted and a low elastic modulus of ~ 5 MPa was observed (typical of composite propellant) and when we use that number to calculate the apparent piezoelectric coefficient, d<sub>33</sub>, a value of ~2000 pC/N is calculated. This is higher than PZT and represents the first time the materials community would consider HTPB bound materials for responsive materials. In fact, even if a conservative value is taken to account for experimental error the apparent piezoelectric coefficient is considered to be giant.*

**Table 1.** Transverse Flexoelectric coefficient for HTPB bound samples with and without AP/MgB<sub>2</sub> inclusions.

Material	Transverse Flexoelectric Coefficient (nC/m)
HTPB nonporous	5.0 +/- 0.6
HTPB porous	6.8 +/- 0.7
HTPB/AP 80 wt% solids	14.5 +/- 1.9

HTPB/AP/MgB <sub>2</sub> (20/75/5 wt%)	11.9+/- 1.3
HTPB/AP/MgB <sub>2</sub> (20/70/10 wt%)	12.2 +/- 0.1
HTPB/AP/MgB <sub>2</sub> (20/65/15 wt%)	11.4 +/- 0.4

We have conducted microCT on the host of samples and have observed what we would consider excessive porosity (Figure 3) for burning rate measurements (at pressure) and therefore we are in the process of remaking these samples and sending them to our collaborators for analysis. These samples will be sent to Travis Sippel to conduct pressurized burning rate measurements. We have done atmospheric burning rates of these materials and the nominal burning rates are on the order of 3 mm/s regardless of MgB<sub>2</sub> loading. Upon ignition, there is clear indication of green light emitting products (BO<sub>2</sub> and other) indicating combustion of MgB<sub>2</sub>.



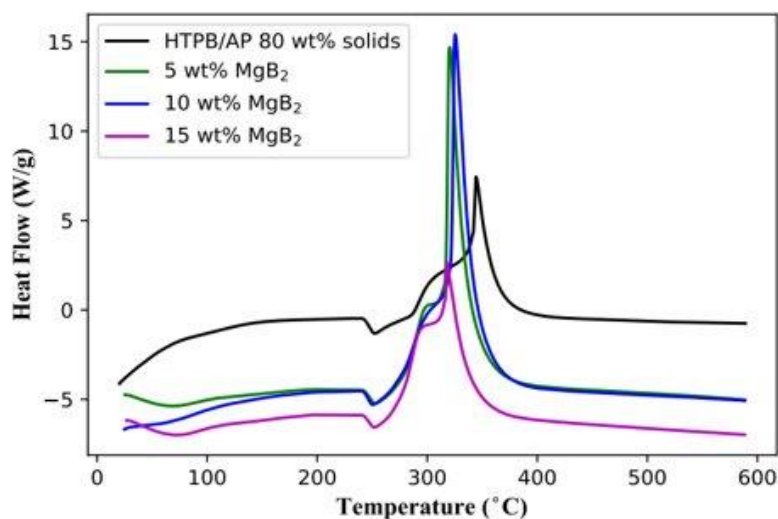
**Figure 3.** Micro CT of HTPB/AP/MgB<sub>2</sub> composite (20/65/15) showing the pores within the sample.



**Figure 4.** Still image of atmospheric combustion of HTPB/AP/MgB<sub>2</sub> (20/70/10 wt%).

Thermal analysis of these formulations via DSC indicates that MgB<sub>2</sub> acts as a catalyst for the decomposition of ammonium perchlorate as there is a clear shift in the onset of reaction and an

increase in the peak energy output as shown in Figure 5. We are presently completing studies with just ammonium perchlorate and  $\text{MgB}_2$  so that we can assess catalytic effects.



**Figure 5.** DSC heatflow data for HTPB/AP/ $\text{MgB}_2$  loaded composite propellant.

#### Major findings for YR 3 include:

- Reactive composites of THV/ $\text{MgB}_2$  exhibit strong flexoelectric behavior and are demonstrated to be responsive in nature (true “smart” material).
- Nanosized PVDF acts as a polarizable inclusion material and can significantly enhance the flexoelectric effect in composite reactive structures. The synthesis route/method results in high beta-phase material and represents a unique method for achieving nanosized electroactive inclusions.
- $\text{MgB}_2$  is found to be an exceptional inclusion material in composite propellant formulations and acts as a fuel as well as a catalyst for the decomposition of ammonium perchlorate.

**Presentations:** This year we plan on presenting at both the GRC Energetic Materials and the International Pyrotechnics Symposium.

1. “Flexoelectricity in Reactive Systems”, **M.J. Zaitzeff\*** and L.J. Groven, Proceedings of the 45<sup>th</sup> International Pyrotechnics Symposium, Colorado Springs, CO, July 10-15<sup>th</sup>, 2022.
2. “An Exploration of Molecular Perovskites for Composite Propellant Applications”, **S.M. Rugh\*** and L.J. Groven, Proceedings of the 45<sup>th</sup> International Pyrotechnics Symposium, Colorado Springs, CO, July 10-15<sup>th</sup>, 2022.

#### Papers:

1. Zaitzeff, M.J.\* and Groven, L.J. (2022), Flexoelectricity in fluoropolymer/aluminium reactives. *Polym Int*, 71: 829-836. <https://doi.org/10.1002/pi.6353>
2. Zaitzeff, M.J.\* and Groven, L.J., Crash precipitation of nanoscale  $\beta$ -phase PVDF particles, *Material Letters*, 330, <https://doi.org/10.1016/j.matlet.2022.133221>

3. Zaitzeff, M.J., and Groven, L.J., Flexoelectricity and Piezoelectricity in MgB<sub>2</sub>/Fluoropolymer Reactives. *J. App. Phys.*, in preparation.
4. Shin, J, Zaitzeff, M.J., Groven, L.J., Zhou, M., Microstructure Enhancement of Macroscopic Flexoelectric Behavior of THV/Al Composites, *J. Appl Phys.*, in preparation.

**Personnel funded:** One full time PhD student, Mikel Zaitzeff, and one full time MS student funded from this effort. Summer salary for PI. Part time undergraduate support during summer.

**Year 4+ (NCE year +) Efforts:**

The primary goal for our year four efforts will be focused on completing detailed studies of MgB<sub>2</sub>, Boron, and crystal inclusions. We will also downselect a composite system for demonstrating as a smart reactive.

Research Thrusts and Tasks	Year 1				Year 2				Year 3				Year 4 +
	1	2	3	4	1	2	3	4	1	2	3	4	
<b>Synthesis &amp; Fabrication</b>													
Milled fluoropolymer/fuel particles													
Fluoropolymer coated fuel particles													
Polymer coated burning rate enhancers													
Polymer coated crystals and composite structures													
Synthesis of energetic perovskites													
Fabrication of composites with downselected inclusions													
FDM of fluoropolymer for enhanced piezoactive phase													
<b>Material Characterization</b>													
Structure & Morphology													
Reactivity, thermal characteristics													
Dielectric properties													
Piezoelectric properties													
Flexoelectric properties													
<b>Performance Characterization</b>													
Design of relevant experiment from Thrust 2													
Field Activated Combustion													
Localized Ignition of Functionally Graded Materials													