



Promoting aluminum nanoparticle ejection from HTPB via exothermic polymer-bound mesoparticles

Erik Hagen[✉], Lei Yang, Yuan Qin, Sammed Bhalerao[✉], Mahbub Chowdhury, Yuxin Zhou[✉], Michael R. Zachariah^{*}

University of California, Riverside, CA, 92521, United States

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ABSTRACT

The incorporation and subsequent ejection of aluminum nanoparticles (nAl) from hydroxyl-terminated polybutadiene (HTPB) remains a significant challenge due to the high specific surface area of nAl and strong interfacial interactions with the polymer matrix. We demonstrate that one approach to facilitate particle removal is the assembly of nAl into mesoparticles (MPs). MPs are micron sized composite particles bound by a polymer binder. In this work, nAl mesoparticles were fabricated using nitrocellulose (NC), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and polypropylene carbonate (PPC) binders and evaluated for their ability to eject nAl from regressing HTPB. MPs formulated with NC and PAN successfully ejected nAl and supported consistent fuel regression. While, in contrast, PVDF and PPC based MPs did not. The observed behavior is attributed to the exothermic decomposition of NC and PAN, which provides localized heat release at the HTPB-MP boundary that enhances the pyrolyzation of surrounding HTPB, generating gas and thereby promoting particle ejection.

Novelty and significance statement: This work introduces a unique strategy for enabling aluminum nanoparticle (nAl) utilization in air-breathing polymer fuels. This is done by synthesizing micron scale mesoparticles made up of nAl and a polymer binder and incorporating them into HTPB. The use of mesoparticles provides two fundamental advantages. The first, is given the choice of binder, properties like gas generation, local oxidation of nAl from decomposition products and decomposition enthalpies can be quantified and used to explain an ejection mechanism. The second, is due to the low surface areas of mesoparticles, high loadings of nAl can be incorporated into the polymer fuel grains. These findings provide a mechanistic insight into nanoparticle ejection, as well as a practical significance for increasing the energy density of air-breathing propulsion systems.

1. Introduction

Increasing the energy density of polymeric solid fuels through the incorporation of energy-dense metal powders is of significant interest for propulsion applications. Hydroxyl-terminated polybutadiene (HTPB) is the defacto standard fuel for solid-fuel applications, and as a binder in propellant systems. To boost energy density aluminum is the most common metallic additive due to its abundance, low cost, and high energy density. Aluminum possesses a volumetric energy density of approximately 84 kJ cm^{-3} , which is substantially higher than that of HTPB (34 kJ cm^{-3}), [1–3] and as a result, the addition of aluminum increases both the overall energy density of the composite and the flame temperature [4,5]. For propellant applications, along with aluminum powder, ammonium perchlorate (AP) is commonly added [6] as the oxidizer. For many desired applications, air-breathing propulsion is

preferred to boost energy efficiency [7–9]. The addition of aluminum to HTPB is not without technical challenges however. For example, nano-scale aluminum (nAl) additives result in an inability to sustain combustion. During regression tests, nAl agglomerates get stuck on the burning surface rather than ejecting, resulting in a layer that eventually quenches the reaction [10]. The inability for nAl to eject from the surface is attributed to a lack of gas generation from the pyrolyzing HTPB to create sufficient lift, and high interfacial forces between the oxide layer in aluminum nanoparticles and HTPB [10].

Two strategies have recently shown some success to enable nAl particles to eject from regressing HTPB in counterflow studies. The first involves the use *in-situ* synthesized nano-scale aluminum particles within HTPB with no oxide passivation layer [11]. The other approach involves coating commercial nAl with a thin copper layer [12]. This strategy focused on triggering eutectic melting, which was confirmed by

* Corresponding author.

E-mail address: mrz@engr.ucr.edu (M.R. Zachariah).

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in-situ TEM, showing Al being extracted from the oxide core below the aluminum melting point [12]. Both studies postulated that back diffused CO₂ and H₂O from the flame, was responsible for exothermic metal oxidation reactions resulting in the HTPB pyrolysis in the neighborhood of the particles, and creating an additional lift impulse to eject the particles.

In this paper we consider another approach. In prior work, we have shown that mesoparticles, which are composite particles comprised of nano-scale fuel powders that are held together by a gas-generating binder, typically nitrocellulose (NC), are more reactive than their physically mixed counterparts [13,14]. The fabrication of composite aluminum-based particles for propellant applications has received considerable recent attention, with several studies demonstrating that solvent evaporation self-assembly methods can produce well-structured Al/AP-based composite particles with intimate contact between components. These works have explored a variety of additive strategies, including fluoride-containing compounds, to engineer the particle's architecture and reactivity [15–18]. While these studies are conducted in AP-containing propellant systems and are primarily concerned with Al combustion performance rather than particle ejection, they collectively demonstrate the broad interest in moving beyond physical mixing toward engineered composite particle designs.

Mesoparticles show an advantage over physically mixed systems for two reasons. The first is the gas generation of the binder, and the second is the synthesized particles are micron scale. Studies show that incorporating nanoparticles into mesoparticles can enhance reactivity in thermite and propellant systems as well [19,20]. *In-operando* microscopic studies of nAl/NC (10–25 wt% NC) MPs performed by Zhou et al. [21] showed that the mesoparticles exploded, which promoted individual particle combustion. This confirmed the theory from Jacob et al. [13] that nAl/NC MPs show reduced burn times due to smaller aggregates being created from MPs explosion.

The strategy of using NC as the binder for mesoparticles, relates to its energetic and low-temperature gas generating properties, which produce an aggressive oxidizer, NO₂ [22,23]. This polymer exhibits two properties that could potentially serve as places that heat can be generated in order to pyrolyze the surrounding HTPB to aid in particle removal. In order to test whether one, both or neither of these properties are necessary to remove particles, three other polymers were chosen. Polyacrylonitrile (PAN), was chosen for its interesting property of exothermic decomposition, similar to NC, but does not contain any oxygen in the polymer [24]. The second polymer is polyvinylidene fluoride (PVDF), which has already found application as a polymer binder for propellants and thermites [25]. PVDF can also act as an oxidizer for Al given its production of HF, which also will etch the alumina shell [26, 27]. PVDF also exhibits endothermic decomposition, as opposed to NC [28]. Lastly, polypropylene carbonate (PPC) was chosen given that it is an unzipping polymer [29] (endothermic decomposition) but produces no oxidizing products. PPC when employed as a polymer binder in thermites has demonstrated significant increases in thermite burn rates over PVDF and has been attributed to its enhanced gas generation [30]. The properties being investigated are summarized in Table 1.

Table 1

Matrix of polymer binder in mesoparticles and their relevant properties being tested.

	Exothermic Decomposition	Endothermic Decomposition
Oxidation Reaction	nAl/NC	nAl/PVDF
No Oxidation Reaction	nAl/PAN	nAl/PPC

2. Methods

2.1. Materials

Nanoscale Al (~80 nm, ~68 wt% Active) was obtained from Nova-Centrix. SEM and TGA/DSC curves can be seen in Figure S2. A nitrocellulose (NC) colloid solution (4–8% in ethanol/diethyl ether) was obtained from Millipore Sigma and was dried to obtain solid nitrocellulose for further processing. Polyvinylidene fluoride (PVDF, average molecular weight: ~534,000) and polyacrylonitrile (PAN, average molecular weight: ~534,000) were purchased from Sigma-Aldrich. Polypropylene carbonate (PPC, QPAC®) was purchased from Empower Materials. N,N-dimethylformamide (DMF), 2-propanol (IPA), anhydrous diethyl ether (99.9%) and acetone were purchased from Fischer Scientific. Hydroxyl-terminated polybutadiene (HTPB, OH value 0.81, measured by the vendor), methylene diphenyl diisocyanate (MDI, modified curing agent), and isodecyl pelargonate (IDP) plasticizer were purchased from Rocket Motor Components.

2.2. Formulation and spray drying of mesoparticle composites powders

Details about the precursor and spray drying formulation can be found in previous publications and an example of the process can be seen in Fig. 1 [19,21]. Precursors were prepared by dissolving the desired amount of polymer (NC, PAN, PVDF or PPC) binder in DMF. After the polymer had dissolved, IPA, acetone and Al NPs or alumina NPs were added to the solution and sonicated for ~1 hr. The final volume ratio of DMF:IPA:acetone is 3:5:2. They were then stirred for a minimum of 24 h. Spray drying was conducted using a Büchi B-290 Mini Spray Dryer in conjunction with a B-295 inert loop. Preheated argon (T~110 °C) was used throughout the system. The prepared suspension was fed through a peristaltic pump at a 45% feeding rate (~12.5 mL min⁻¹) with an aspirator rate of 85% (~33 m³ h⁻¹) and ~7 L min⁻¹ of inlet gas flow. The resulting slurry was shear mixed, and sonicated during the process of spray drying. The particles were collected in a cyclone-based collector, which was electrostatically neutralized before sample collection.

2.3. Fuel grain preparation

A detailed formulation of each composition can be found in Table 3. Typically, ~1568 mg of HTPB, ~232 mg of MDI and ~200 mg of IDP were mixed for 5 mins at 2000 RPM in a mixer (Thinky AR100). Then

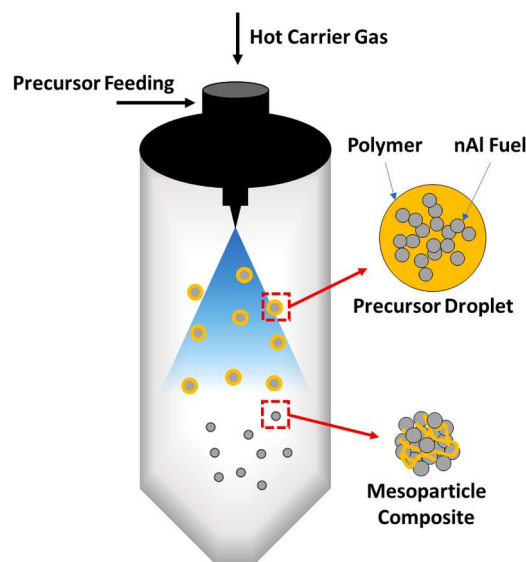


Fig. 1. Spray drying assembly of the nAl/polymer mesoparticles.

nAl/polymer MP powders were added and stirred for 10 mins at 2000 RPM. The resulting paste was then extruded into a 1 mL syringe (ID ~ 4.8 mm) and left to cure for three days. After curing, the strands were then removed from the molds and cut into $\sim 1\text{--}1.5$ cm grains.

2.4. High-speed imaging and temperature measurements

High-speed color imaging was performed at two different magnification levels to investigate both macroscopic and microscopic combustion events, and is described in detail in a previous publication [31]. Macroscopic imaging used a Phantom Miro 110 camera with a Nikon AF Micro Nikkor lens (aperture set at $f/16$, spatial resolution ~ 30 $\mu\text{m pixel}^{-1}$), while microscopic views employed a Phantom VEO710L camera coupled to a long working distance microscope lens (Infinity photo-optical model K2 DistaMax, CF-4 objective), which provides a spatial resolution of ~ 2.1 $\mu\text{m pixel}^{-1}$, from a working distance of ~ 54 mm. Each camera's framerate and exposure time used can be seen in Table S1. An overview of multi-spectral pyrometry [32] and details of our three-color pyrometry [33,34] can be found in previous studies. Briefly, a custom MATLAB script extracts and demosaics the color images based on the three-color channels (red, green and blue) and the camera's Bayer filter respectively. Ratios of the light intensity (G/R, B/G and B/R) are used to estimate the temperature at that pixel. The system was calibrated with a blackbody source (Mikron, Oriel) with an uncertainty of $\sim 200\text{--}300$ K.

2.5. Counterflow burner and regression rate

Combustion evaluations of the fuel grains were conducted in a counterflow configuration. Details of our burner can be found in a previous publication [11]. The velocity and temperature of the air are controlled by a mass flow controller (MKS model 1179, and 247D 4-channel readout) and a resistive heating tube (Omega 316 SS inline duct heater), thermocouple (K-type), PID (Inkbird) relay. The final velocity of the air through the ~ 19 mm diameter nozzle ($3/4''$) was calculated by applying a density correction to the initial volumetric flow rate of the air. A series of six stainless steel mesh disks, three coarse and three fine, (McMaster, 40×40 then 100×100 mesh disks, model 9317 T552 and 9317 T555) were placed at the 19-mm-diameter nozzle exit to collimate the airflow. To keep the separation distance between the fuel grain's surface and the exit nozzle constant, a laser-photosistor feedback loop driving a stepper motor (Thorlabs DRV225 with BSC201 controller) via an Arduino Uno microcontroller board and custom C# script. Prior to ignition, the stepper motor retracts, and a fuel grain is loaded into the burner. The laser is positioned ~ 2 mm above the top of the burner and aligned with the photosistor. The motor then extrudes until the laser line is interrupted by the fuel grain, setting the initial height. During combustion, the signal from the photosistor is tracked, and the fuel grain is extruded once the signal threshold is reached. After each run, the recorded time and position data are fit to a linear curve, where the slope, or the extrusion rate of the stepper motor, gives the regression rate of the fuel grain. A schematic can be seen in Figure S1.

2.6. TGA-DSC, TOFMS and SEM

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a NETZSCH STA 449 F3 Jupiter. Approximately 3 mg of sample powder was loaded into an alumina crucible and heated from room temperature to 770 K at 1 K min^{-1} under a continuous flow of high-purity Ar (50 mL min^{-1}). T-jump time-of-flight mass spectrometry (TOFMS) on HTPB with metal or metal oxide additives was performed at a heating rate of 3.5×105 K s^{-1} under high vacuum ($\sim 10\text{--}6$ Torr), following the same procedure described in detail elsewhere [35,36].

Scanning electron microscopy (SEM, Thermo-Fisher Scientific NNS450) coupled with energy dispersive X-ray spectroscopy (EDS) was

used to analyze the spray dried mesoparticles before combustion.

3. Results and discussion

3.1. Polymer binder and mesoparticles characterization

Four polymers with different properties as discussed above were chosen as binders for the mesoparticles (MPs). The polymers were chosen based on whether their decomposition is exothermic or endothermic and whether or not oxidizing species are generated from decomposition. To assess the heat released during decomposition, DSC/TGA experiments were conducted on the neat polymers in Ar. Fig. 2(a) shows DSC and TGA traces for the polymers. Nitrocellulose (NC) and polyacrylonitrile (PAN) both show exothermic decomposition at temperatures of ~ 195 and 280 $^{\circ}\text{C}$ respectively. On the other hand, polyvinylidene fluoride (PVDF) and polypropylene carbonate (PPC) show endothermic decomposition at ~ 425 and 230 $^{\circ}\text{C}$ respectively. PVDF also shows a melting step at ~ 150 $^{\circ}\text{C}$. The other property of interest is the production of oxidizing species during the polymer's decomposition. Both NC and PVDF can form oxidizing species. TOFMS for the four polymers can be seen in Fig. 2(b). NC partially decomposes into NO_2 ($m/z=46$) and PVDF forms HF ($m/z=20$). Both of which can be used to oxidize the Al. Evidence of the MPs reacting with the oxidizing species is seen by the detection of Al_2O (Figures S12 and S13) and AlF. Using PVDF as an oxidizer has been explored in previous publications [37–39].

The spray drying process allowed for micron scale composite mesoparticles (MPs) to be assembled and are comprised of nano scale aluminum (nAl) held together by one of the chosen polymers, to create a super-micron near-spherical aggregate. Two different loadings (10 and 25 wt%) were chosen for this study to see the effect of polymer loading in the fuel grains. For PPC, only MPs at 25 wt% polymer was considered due to their lack of reactivity which will be discussed later. To ensure that there are no drastic changes in the seven different MPs, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) images were analyzed to assess composition, morphology and diameter.

Composition was assessed through TGA measurements carried out in Ar to ensure the composition of each mesoparticle formulation was close to the initial mass loading of each component. This also simulates the anaerobic environment the MPs would be subject to on the surface of the HTPB during regression studies. The initial mass drop in the TGA is assumed to be the polymer content of each MP. TGA curves can be seen in Figure S6, and a table of the initial mass drops can be seen in Table S2. All mass drops are less than the considered amounts with MPs with 10 wt% polymer within 2–4 wt% and those with 25 wt% polymer within 5 wt%. We believe this is due to char left behind by the polymers. The exception to this is PAN, which only shows a 6 and 4 wt% drop for each loading respectively. We believe this is due to the significant char left behind during decomposition Fig. 2(a), owing to its use as a precursor for carbon fiber synthesis [40–42].

The left-hand column of Fig. 3 shows SEM images for the synthesized MPs with mass loadings of 75/25 wt% and the right-hand column shows size distributions of MP diameters for both 90/10 and 75/25 wt% nAl/polymer. SEM images show that the MPs are mostly spherical and discrete particles. There were not many visual changes between the two polymer loadings and SEM images can be seen in Figure S3 along with high magnification EDS images in Figures S4 and S5 (10 and 25 wt% polymer respectively). EDS shows that there is a homogenous distribution of Al and the polymers across the surface. Diameters were taken by manually estimating the diameter of a bounding circle for various particles. Details and a sample of this process can be seen in Section S3.3. The diameters of the MPs appear to be lognormal. Averages and standard deviations of the distributions were taken and are displayed in Table 2. Most of the particles ranged from approximately 2–7 μm in diameter. It is interesting to note that increasing the polymer content increased the size of the NC based MPs, while, in contrast, the higher polymer loading decreased the size of the PAN and PVDF based MPs. The

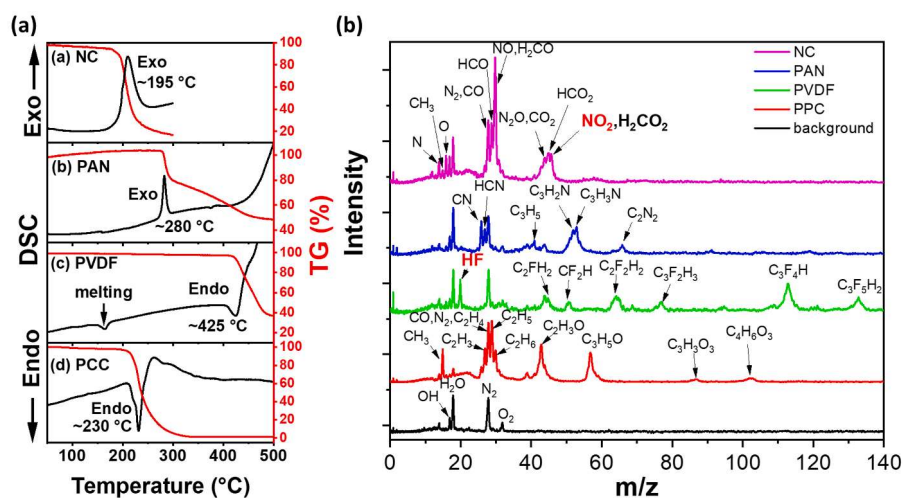


Fig. 2. (a) DSC and TGA traces for NC, PAN, PVDF and PPC polymers. (b) TOFMS for the four polymers. The oxidizing species generated from NC and PVDF are labeled in red.

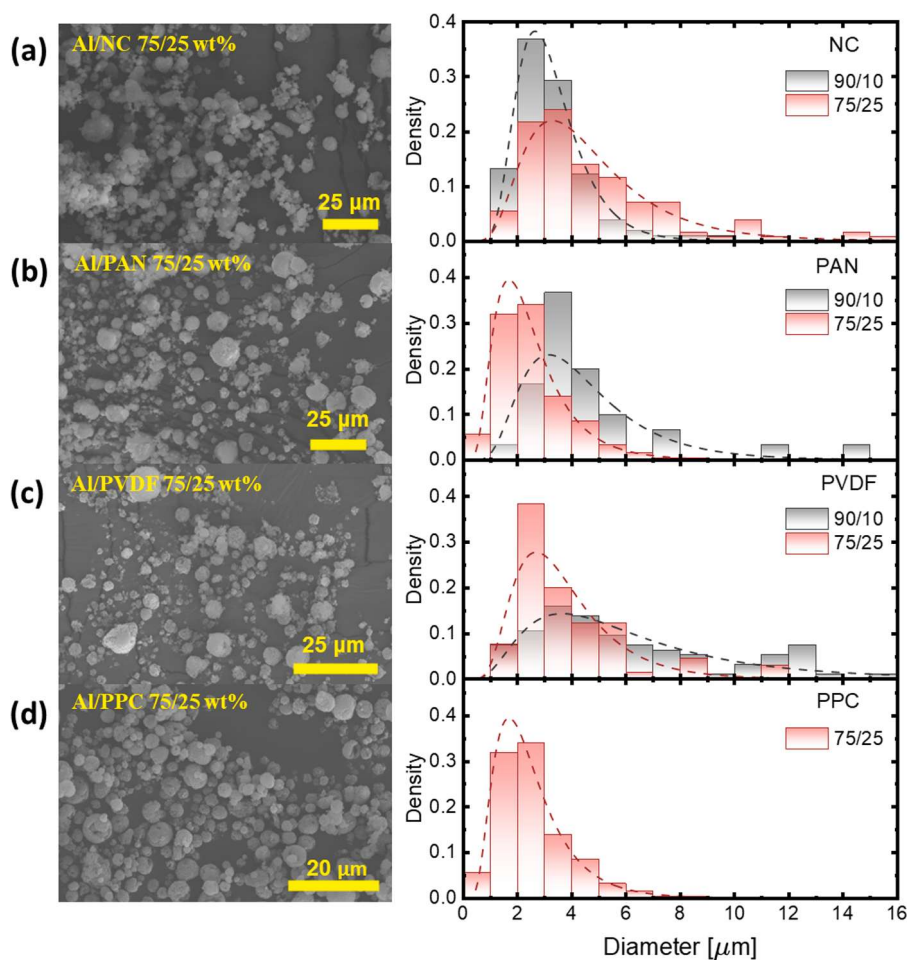


Fig. 3. SEM micrographs of nAl/polymer MPs at 75/25 wt% (left) and corresponding particle diameter distributions (right) for Al/polymer composites. Rows (a–d) correspond to Al/NC, Al/PAN, Al/PVDF, and Al/PPC, respectively. Gray and red histograms denote 90/10 and 75/25 wt% formulations, respectively. The dashed lines denote a lognormal fit.

reason for this is not explored in this report, but might be of interest at a later date.

3.2. Combustion of composite fuel grains

Combustion of HTPB and composite fuel grains was characterized in a counterflow burner. Photographs of combustion of the various grains in the counter flow-configuration can be seen in Fig. 4. All fuel grains

Table 2
Diameters of synthesized mesoparticles.

Polymer wt%	Diameter [μm]			
	NC	PAN	PVDF	PPC
10	3.3 ± 1.4	4.5 ± 2.7	6.5 ± 4.1	-
25	4.8 ± 2.7	2.5 ± 1.3	3.8 ± 2.1	2.5 ± 1.3

were made through a physical mixing process containing various mass loadings of nAl and nAl MPs ranging from 5–25 wt% nAl and 1–8 wt% polymer binder. Tests were carried out with a range of strain rates of 100–300 s⁻¹ and a pre-heat air temperature of ~770 K (500 °C). A table of the fuel grains containing MPs can be seen in Table 3. Measured and theoretical densities were compared to estimate porosities (Tables S5 and S6). All samples showed porosities of ~1–11%.

It is important to note, that in the counterflow configuration, the region between the HTPB's surface and the diffusion flame is nearly anaerobic, comprising of mainly HTPB's pyrolysis products (1,3-butadiene) [43].

During combustion of neat HTPB, the surface is seen to be smooth with a flame offset, tracing the curvature of the polymer's surface (Fig. 4 (a)). The addition of loadings as small as 5 wt% nAl resulted in bright orange spheres forming on the surface of the HTPB due to the lack of particle ejection, and subsequent sintering of the Al nanoparticles (Fig. 4 (b)).

A qualitatively similar outcome was observed for MPs formulated with PVDF and PPC binders (Fig. 4(c) and (d)). Despite some initial ejection events, glowing sintered aggregates eventually accumulated on the surface and quenched the reaction for both PVDF and PPC based MPs at all loadings tested (10/1/89 and 10/3/87 wt% Al/polymer/HTPB). Time scales for the onset of sintering in these systems are provided in Figure S10. Sintering caps began forming at ~1.5 s after fuel grain ignition, full encapsulating the surface by ~8 s. Regression stopped ~1 s after caps were formed on the surface.

In contrast, MPs formulated with NC Fig. 4(e) showed consistent regression at strain rates of $K \geq 200$ s⁻¹. At $K = 100$ s⁻¹, the flame transitioned from the expected surface-offset configuration to an upward envelope geometry, and a black residue accumulated inhomogeneously on the surface, ultimately leading to extinction (Figure S8). At $K = 200$ s⁻¹ all samples showed many ejections with consistent regression at the same loadings as the previously tested PVDF and PPC MPs. The diffusive flame formed during combustion looked similar to the flame of the neat polymer. This flame was disturbed upon the ejection of particles from the surface. The surface of the regressing composites looked jagged, instead of smooth.

MPs formulated with PAN binder (Fig. 4(f)) also promoted particle

ejection, but steady regression was only sustained at the highest strain rate tested, $K = 300$ s⁻¹. Below this strain rate, a crust formed on the HTPB surface and eventually extinguished the reaction, with the exception of partial propagation observed for the 75/25 wt% nAl/PAN formulation at 25 wt% total nAl loading at $K = 200$ s⁻¹ (Figure S9). The flame and surface morphology during steady combustion of nAl/PAN MP fuel grains were similar to those observed for nAl/NC MP fuel grains.

Given the micron scale diameter of the particles, higher loadings of nAl could be mixed into the HTPB than would be previously allowable. Empirically, a maximum loading of only ~15 wt% of the ~80 nm Al can be added to HTPB, before the resulting paste is not extrudable due to the high specific surface area of nAl. Since the MPs have micron scale diameters, a maximum of 25 wt% nAl (~28 wt% MPs) was able to be loaded into the uncured HTPB while still allowing for an extrudable paste. The higher loading of MPs resulted in an increase in ejections from the surface allowing for more reliable high-speed microscopic imaging. Snapshots of ejections captured with the microscopic lens can be seen in Fig. 5. Both NC and PAN based MPs showed similar types of ejections either as a cluster of small ejecta, or large micro-scale particles. NC routinely showed a higher frequency of smaller ejections. Three color pyrometry revealed that the temperature of these ejections ranges anywhere from 2000–2500 K. For comparison, pyrometry was also conducted on the macroscopic images and showed temperatures of ~2800 K (Figure S11), which is close to what is seen on the microscopic camera and aligns well with previous measurements of burning Al droplets [31,44,45].

While three-color pyrometry provides a useful estimate of the condensed-phase particle temperature, it is important to note that it does not fully capture the temperature of the surrounding gas-phase flame. Spectroscopic measurements and calculations estimate that the flame temperatures including Al particles can exceed 3000 K [46,47]. While actual motor environments exhibit these elevated temperatures, it should be noted that the counterflow configuration is not a useful tool for measuring the effect of elevated flame temperatures driven by particle combustion. In this geometry, the ejected particles combust at a significant distance (>2 mm) from the HTPB surface. Generally, the

Table 3
Mass loadings of the various components in the fuel grains.

Mesoparticle	Fuel Grain		
nAl/Polymer wt%	Al wt%	Polymer wt%	HTPB wt%
90/10	10	1	89
	25	3	72
75/25	10	3	87
	25	8	67

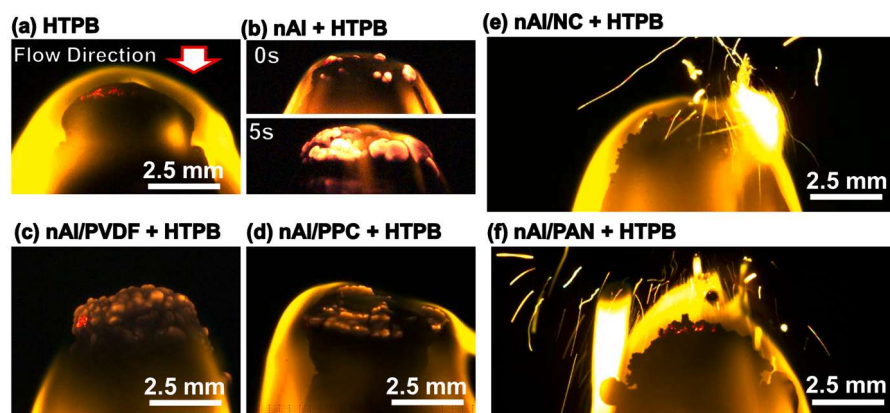


Fig. 4. Color images of the fuel grains regressing in the counterflow at $K \approx 300$ s⁻¹. (a–f) show macroscopic images of the HTPB and physically mixed nAl or mesoparticle composites.

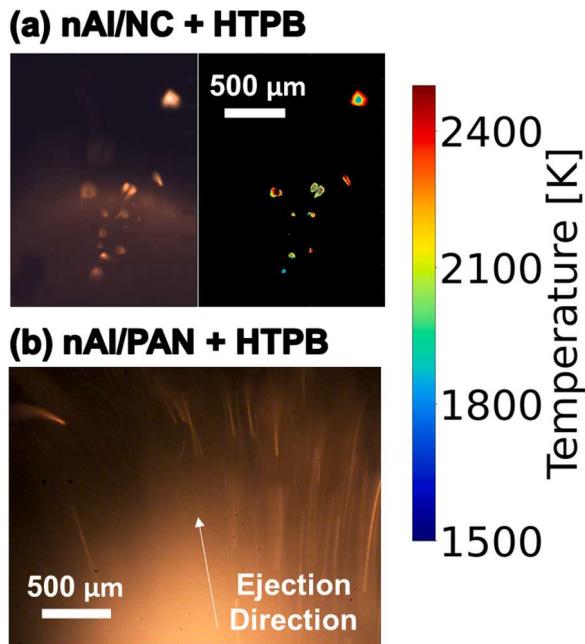


Fig. 5. Microscopic snapshots and false color temperature maps of particle ejections from nAl/NC MPs (a) and nAl/PAN MPs (b).

inclusion of embedded particles enhances the regression rate of solid fuels and propellants by elevating the global flame temperature, which subsequently increases the heat flux to the regressing surface [48,49].

3.3. Regression rates

Along with high-speed imaging, regression rates of the fuel grains were measured across the range of strain rates at a constant air temperature of ~ 770 K. Fig. 6 shows the regression rates of neat HTPB and fuel grains containing 10 wt% nAl (Fig. 6(a)) and 25 wt% nAl (Fig. 6(b)). The regression rate of the HTPB rose from ~ 0.15 mm s $^{-1}$ to ~ 0.3 mm s $^{-1}$ as the strain rate increased from 100 s $^{-1}$ to 300 s $^{-1}$. To evaluate the performance of the NC and PAN based mesoparticles, the regression rates of four configurations were evaluated. Table 3 shows details about the nAl and polymer loadings from the two different mesoparticles into the fuel grains. Due to there being no consistent regression at $K = 100$ s $^{-1}$, for either the NC or the PAN, no data points for the MPs are shown. nAl/PAN/HTPB fuel grains with a loading of 25/8/67 wt% showed partial regression before sintering at $K = 200$ s $^{-1}$ and that partial regression is shown in Fig. 6(b), but labeled as partial regression.

At 10 wt% nAl MP in the fuel grain, the NC based MPs regressed at a similar rate to HTPB, while the PAN based MPs showed a lower regression decreasing ~ 50 – 60% when compared with HTPB. Both MPs showed little to no change when increasing the polymer from 1 to 3 wt% in the overall fuel grain at low MP loadings. At higher loadings of the MPs to achieve 25 wt% nAl in the samples, the MPs comprised of 90/10 wt% nAl/polymer and did not exhibit much change in regression. In contrast, the addition of ~ 8 wt% of polymer in the sample, increased the regression rates of both the NC and the PAN based MP to ~ 0.4 mm s $^{-1}$ and ~ 0.25 mm s $^{-1}$ respectively. To summarize, changing the polymer loading in the fuel grain from 1 to 3 wt% did not significantly affect the regression rate. However, once there was ~ 8 wt% polymer, the regression rates increased. This suggests that the system must be sensitive to the polymer loading in the overall composite, and not necessarily just in the MP. MPs with 25 wt% nAl (Al/NC=75/25), a loading unachievable without an MP formulation, showed significantly higher regression rates.

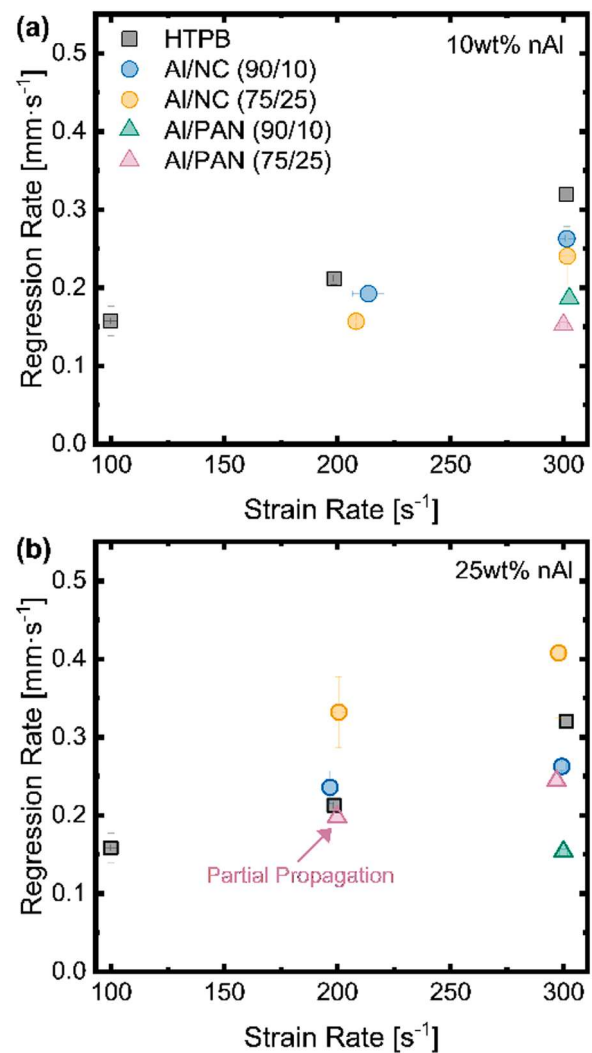


Fig. 6. Regression rates for mesoparticle/HTPB fuel grains containing 10 wt% (a) and 25 wt% (b) nAl in the composite. Circles correspond to Al/NC mesoparticles and triangles correspond to Al/PAN mesoparticles. Mesoparticles did not propagate at a strain rate of 100 s $^{-1}$.

3.4. Mesoparticle ejection mechanism

Given the enhanced regression of some mesoparticle systems we now consider why the NC and PAN based MPs eject nAl particles while the others do not. To reiterate, the environments the MPs are subject to are oxygen deficient and mainly comprise of gasses created by HTPB pyrolyzing.

Zhou et al. postulated that the decomposition of the polymer binder in the mesoparticles would generate gas, and therefore remove the particles from the surface of the HTPB [10]. Following from [10], the maximum possible work (W_{max}) done by the polymer in the mesoparticle decomposing was computed. Since all the mesoparticles have similar diameters, this calculation relies only on the pressure (P) estimated from the polymer decomposition. It should be noted that this calculation assumes that the polymer decomposes only into its monomer, which means the number of products (n) is underestimated. This means that we are likely also underestimating the pressure ($P \propto n$) and maximum work ($W_{max} \propto P$) as a result. More details can be found in the supplemental information in Section S7. From these calculations, PVDF expresses the highest maximum work followed by PAN, PPC and NC in order of descending work. This trend can be seen in Fig. 7. This is due to the low molecular weight of PVDF. Given that the NC based MPs

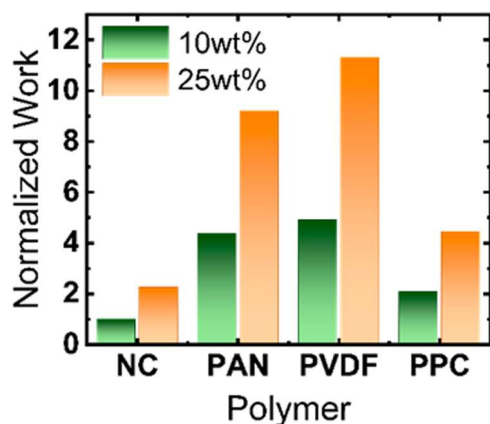
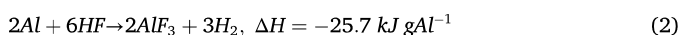
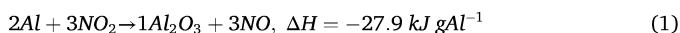


Fig. 7. Normalized work done by mesoparticle polymer decomposition. Every point was normalized relative to NC at 10 wt% polymer.

propagated, this calculation would suggest that all polymers should eject particles from the HTPB's surface, which is not the case for the PVDF and PPC. PPC is considered an unzipping polymer [50,51] and has been used as a gas generator to increase the burn rates of thermite/polymer composites [30]. If gas generation was the only method for particle ejection, then polymers like PPC should be good candidates. This means there is a different mechanism controlling nAl ejection during regression.

In our previous publications regarding nAl ejection from HTPB [11, 12], it was postulated that back diffused H_2O and CO_2 initiated partial oxidation of the aluminum on the surface and transferred heat into the surrounding HTPB. This pyrolyzed the polymer and generated enough gas to eject particles from the surface. This theory states that there has to be some local exothermicity in order to generate enough gas to remove the nAl. Local exothermicity can come from two different sources: oxidation of the nAl from the MP's polymer decomposition; and exothermic decomposition of the polymer. PPC does not generate any oxidizing species upon decomposition and exhibits endothermic decomposition (Fig. 2), which is likely why the PPC MPs do not eject nAl and combustion is eventually extinguished.

Heat flux into the HTPB can also come from the MP polymer binder's decomposition producing oxidizing species. To explore the possibility of local oxidation, time of flight mass spectroscopy (T-Jump MS) was carried out on both neat NC and nAl/NC MPs, and presented in Figures S10 and S11. The neat polymer showed a peak at $m/z=46$ suggesting the production of NO_2 which can act as an oxidizer for the aluminum. Traces of the nAl/NC MPs show the production of Al_2O ($m/z=70$) which is absent for NC and MPs synthesized with nAl_2O_3 and NC. Al_2O has been shown to be the main intermediate oxidation product from Al/CuO thermite reactions [52]. As a result, it is assumed that the NO_2 is partially oxidizing the Al in the MPs. This is further confirmed by the decrease in the ratio of the NO_2 peak and the HCO ($m/z=29$) peak in the nAl/NC MPs relative to neat NC. The reaction between Al and PVDF has been studied previously, and the reaction mechanism has been probed [27]. TOFMS shows that the HF gas generated from PVDF can act as an oxidizer for the Al fuel [26–28]. The HF also has interesting pre-reaction chemistry with the passivation shell of the nAl, etching the surface [28,53]. Calculated enthalpies of both reactions are summarized in Eqs. (1) and (2) using Al mass base to normalize them. Since they are essentially equivalent and given that the PVDF based MPs did not propagate, it is likely that this is not exothermic enough to generate gas from HTPB pyrolyzation.



There are some other reasons for lack of reactivity of the PVDF based mesoparticles. First, PVDF will melt at $\sim 150^\circ\text{C}$ as seen in Fig. 2(a), while the surface temperature of HTPB has been estimated with IR imaging to be $\sim 500^\circ\text{C}$ [12], which is well above PVDF's melting temperature. Thus, MPs may be destroyed well below the HTPB surface allowing the nAl to agglomerate into large aggregates, subsequently leading to similar problems outlined for nAl/HTPB composites. Second, previous studies place the ignition temperature of Al/PVDF at $\sim 800^\circ\text{C}$ in Ar, [54] which is much higher than the estimated HTPB surface temperature of 500°C . Lastly, the HF could be consumed by the alumina shell before having a chance to react with the Al core. DSC measurements notice exothermic peaks of nAl/PVDF composites around $350\text{--}600^\circ\text{C}$ with enthalpies of $\sim 20\text{--}200 \text{ J g}^{-1}$ [37,38]. This value is lower in magnitude than the HF reacting with just Al. These three factors when combined would argue that there is never any ignition, and the HF gas generated by the PVDF decomposition is carried away with the HTPB's pyrolysis products.

The second property of interest that takes place when the polymer in the MP decomposes is whether or not the process is exothermic or endothermic. Both the NC and PAN polymers exhibit exothermic decomposition and integrating under the exothermic peaks of the DSC traces (Fig. 2(a)) for both yields an exothermicity of $\sim 1650 \text{ J g}^{-1}$ for NC and $\sim 230 \text{ J g}^{-1}$ for PAN. Thus, NC releases $\sim 7 \times$ more energy than PAN. To evaluate the maximum possible HTPB that can be volatilized from the decomposition of these two polymers in the MPs, a simplified energy balance approach is employed. This framework is similar to previous works [11,12]; however, instead of using single Al particles, a single mesoparticle is used.

To start, the density of the MPs needs to be estimated. The density of a dense particle (ρ_{dense}) made up of nAl and either polymer can be estimated with the following equation:

$$\rho_{dense} = \left(\sum_i \frac{w_i}{\rho_i} \right)^{-1} \quad (3)$$

where w_i and ρ_i are the mass fractions and densities of each component, respectively. However, mesoparticles consist of loosely packed aggregates and therefore exhibit internal porosity. While no measurements of a single MP's porosity have been conducted, Zangmeister et al. [55] estimate the packing density of rigid aggregates to be ~ 0.36 , meaning the porosity can be assumed to be ~ 0.64 . Accounting for the porosity (P) the effective MP density (ρ_{MP}) can be estimated using,

$$\rho_{MP} = (1 - P)\rho_{dense} \quad (4)$$

Densities of each component, as well as the dense and porous densities can be seen in the supplemental information in Tables S2 and S4 respectively. Using Eqs. (3) and (4) yields porous densities of $\sim 0.75\text{--}0.95 \text{ g cm}^{-3}$ for the four different MPs.

With the effective MP density established, the maximum volume of surrounding HTPB that can be pyrolyzed during the MP's polymer's decomposition is shown in Eq. (5).

$$\frac{V_{HTPB}}{V_{MP}} = \frac{\Delta H_{decomposition} \rho_{MP} \chi_{poly}}{E_{HTPB} \rho_{HTPB}} \quad (5)$$

where V_{HTPB} and V_{MP} are the volumes of the HTPB and the MPs respectively. $\Delta H_{decomposition}$ is the enthalpy of either of the MP polymers decomposition. Property data used for these calculations can be found in the supplemental Tables S4 and S5. The calculated volume ratios are shown in Fig. 8(a). For Al/NC mesoparticles, the calculated ratios are ~ 1.7 for the 90/10 formulation and ~ 3.9 for the 75/25 formulation, indicating that exothermic NC decomposition can volatilize a volume of surrounding HTPB comparable to, or several times greater than, the mesoparticle volume. In contrast, Al/PAN mesoparticles yield substantially lower ratios of 0.23 and 0.48 for the 90/10 and 75/25 formulations, respectively, suggesting that PAN decomposition alone is

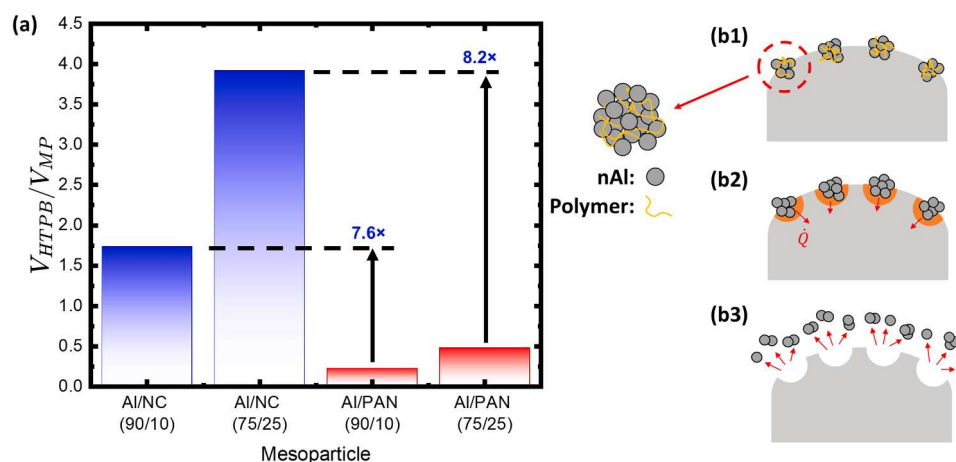


Fig. 8. (a) Maximum volume of HTPB that can be volatilized from a single mesoparticle decomposing. (b1–3) Shows the ejection mechanism. Initially there are mesoparticles on or near the surface (b1). Next, the polymer decomposes and transfers heat into the HTPB (b2). The surrounding HTPB is pyrolyzed and the gas generation from the polymer decomposition and the surrounding HTPB ejects particles from the surface (b3).

insufficient to volatilize an equivalent volume of surrounding binder. These differences we believe explain why fuel grains with NC regress faster than those with PAN, and likely why low PAN loadings do not show continuous regressions at low strain rates.

It should be reiterated that Eq. (5) provides an estimate of the maximum volume of surrounding HTPB that could be pyrolyzed assuming that all of the heat generated from the MP polymer's decomposition is transferred into the surrounding binder. With this in mind, the calculated V_{HTPB}/V_{MP} values for Al/PAN mesoparticles are below unity, but particle ejection is still observed experimentally. This indicates that volatilization of a binder volume comparable to the mesoparticle volume is not a prerequisite for ejection. Rather, localized polymer decomposition at the HTPB-MP interface can generate sufficient gas production and binder softening to reduce adhesion and promote particle removal. In this context, Eq. (5) should be interpreted as an upper-bound estimate of affected binder volume, rather than a minimum threshold for ejection. This interpretation can explain why the PVDF containing MP composites do not propagate. If it is assumed that there is no reaction between the Al and the oxidizing products, there is no heat transfer to the surrounding HTPB and the volume ratio is zero. Given this, the ejection mechanism appears to be governed by exothermic decomposition. The process for nAl removal through exothermic polymer decomposition is demonstrated in Fig. 8(b).

4. Conclusion

This study details a mechanism and criteria, to use MPs as a method eject nAl from a regressing HTPB surface. Four polymers were chosen to probe the ejection mechanism of nAl MPs from a regressing HTPB surface. NC and PAN were chosen for their exothermic decomposition, while PVDF and PPC were chosen for their endothermic decomposition. NC and PVDF generated oxidizing species that could partially ignite the nAl in the MP.

It was found that only MPs containing either NC or PAN could propagate, while PVDF and PPC MPs sintered and eventually extinguished. Due to the micron scale of the particles, 25 wt% of nAl was able to be incorporated into the fuel grains. This is higher than the 15 wt% of the nascent nanoparticles that could be mixed into the HTPB. Regression rates of fuel grains containing 10 wt% nAl showed that NC based MPs regressed similarly to HTPB while PAN based MPs only regressed at ~50% of HTPB. Increasing the loading of nAl to 25 wt% resulted in an increase in the regression rate for nAl/NC MPs and no enhancement for PAN MPs. TOFMS confirmed that both nAl/NC and nAl/PVDF MPs were reacting, but showed similar enthalpies confirming that this is likely not

the candidate for local heat flux. DSC traces revealed that NC's decomposition is almost $7 \times$ as exothermic as PAN's. V_{HTPB}/V_{MP} suggest that heat transfer at the HTPB-MP boundary is dominated by the MP's polymer rather than any exothermic reaction between the nAl and decomposition products. These findings show that MPs can be used to increase the loading of nAl in HTPB and using a polymer binder with exothermic decomposition allows for the nAl to be ejected from the surface during regression studies.

CRediT authorship contribution statement

Erik Hagen: Writing – original draft, Visualization, Methodology, Formal analysis, Data curation. **Lei Yang:** Writing – review & editing, Visualization, Data curation. **Yuan Qin:** Data curation. **Sammed Bhalariao:** Data curation. **Mahbub Chowdhury:** Data curation. **Yuxin Zhou:** Data curation. **Michael R. Zachariah:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Conceptualization.

Declaration of competing interest

On behalf of all the authors, we declare no conflict of interest. This work is original and has not been considered for publication elsewhere.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.combustflame.2026.115314](https://doi.org/10.1016/j.combustflame.2026.115314).

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