Exploring mechanisms for agglomerate reduction in composite solid propellants with polyethylene inclusion modified aluminum

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In composite solid propellants, shortening particle residence time at the burning surface and inducing particle microexplosions could decrease aluminum agglomeration, thus reducing two-phase flow losses in a rocket motor. We explore this by using aluminum particles modified with low-density polyethylene (LDPE) inclusion to drive intraparticle outgassing, which could break apart composite particles, yielding smaller and faster burning fragments during composite solid propellant combustion. We find that use of these particles in a propellant results in more prompt particle ignition, and surface residence time is decreased. For composite propellant burning at 6.9 MPa, mean coarse agglomerate diameter is decreased from 75.8 μm (spherical aluminum) to 29.0 μm (Al/LDPE 90/10 wt.% particles). Thermal analysis with DSC/TGA shows that 10 wt.% LDPE inclusion in aluminum (1.5% of propellant weight) results in enhanced oxidation characteristics that are more similar to nanoaluminum than neat spherical aluminum. Thermochromic equilibrium calculations indicate LDPE inclusion decreases specific impulse by 1.0% from 262.7 to 260.0 s, but it is expected that in a motor, LDPE inclusion could produce a net increase in specific impulse due to a substantially reduced agglomerate size. This work shows that reduced agglomeration is possible using gas generating inclusion materials that are only weakly reactive with aluminum.

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1. Introduction

Increasing the specific impulse performance of solid rocket motors by reduction of two-phase flow losses remains an elusive goal. Two-phase flow losses, which occur from kinetic and thermal non-equilibrium between condensed phase particles and surrounding product gas are prevalent for aluminized formulations. In a typical aluminized composite solid propellant, two-phase flow losses can be significant, resulting in a 3–5% reduction in specific impulse [1,2]. The dissimilarity between propellant burning surface temperature (~500–700 °C) [3] and aluminum particle ignition temperature in a propellant (reported by different authors to vary in the range of 1400–2100 °C) [4–6] is a particular cause for formation of large agglomerates. During propellant combustion, aluminum particles emerge from solid propellant and aggregate at the propellant burning surface. Aluminum aggregates can remain at the burning surface until they reach their ignition temperature, spending a significant amount of time at temperatures above the aluminum melting point. This results in aluminum particle sintering or coalescence into larger aggregates or agglomerates [7–9].

Prior efforts to reduce two-phase flow losses have attempted to reduce product agglomeration by using smaller aluminum particles. Use of smaller, nanoscale aluminum (nano-Al) particles in composite propellant results in shorter burning surface residence time due to faster particle heating and ignition at a lower temperature than micrometer-scale aluminum [10]. Replacement of micrometer-scale aluminum with nanoaluminum can decrease coarse agglomerate size to 2 μm [9,11,12]. However, the high oxide content of nanoaluminum particles (~10–50 wt.%), and poor aging characteristics can reduce propellant specific impulse [13]. Additionally, nanoaluminum’s high specific surface area (~10–50 m2/g) can result in unprocessable viscosities [14] and poor mechanical strength [15], causing motor failure. Consequently, nanoaluminum is not currently used in fielded propellant formulations.

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Additional efforts to reduce agglomeration have focused on overcoming the drawbacks of nanoaluminum by using micrometer-scale particles that undergo low temperature, exothermic reactions to accelerate their ignition and thus reduce burning surface residence time. To this end, metallic [16–19] and polymeric [18,20] particle coatings have been employed to achieve limited agglomeration improvement through exothermic reaction with underlying aluminum cores. Nickel coatings react in the condensed phase to first form nickel aluminides, and in propellant combustion, this was reported to reduce coarse agglomerate size by ~20%, but agglomerates (~122 μm) were still about five times larger than the initial aluminum particle diameter (~22 μm) [17]. Fluoropolymer coatings react with underlying aluminum and aluminum oxide during heating to form an aluminum fluoride coating that upon sublimation at ~1300 °C might aide separation of aggregated aluminum particles at the burning surface. Use of fluorinated coatings (poly(methylfluoroacrylate or fluorocarbon chlorosilanes) [18,20] reduces coarse agglomerate size, however agglomerates are still one and two orders of magnitude larger than initial aluminum particle sizes. In general, since particle coatings act to prevent agglomeration of one aluminum particle with another, coarse agglomerate sizes are limited by the initial aluminum particle size.

Coarse agglomerates smaller than initial particle sizes are theoretically possible if breakup of aluminum at the burning surface can be achieved. Toward this goal, partial replacement of aluminum with mechanically activated Ni/Al reactive particles in a hydroxyl-terminated polybutadiene (HTPB) and ammonium perchlorate (AP) composite solid propellant decreases coarse agglomerate size from 235 to 90 μm (1 atm pressure) [21], but due to the high quantity of nickel present in particles (~70 wt.%), theoretical specific impulse is reduced by ~25 s. Higher theoretical performance is possible through use of poly(tetrafluoroethylene) (PTFE) inclusions within micrometer-scale aluminum particles, which result in only a 2–7 s decrease in theoretical specific impulse [22]. Low level (10–30 wt.%) PTFE inclusion modification was found to expedite aluminum ignition and produce coarse agglomerates smaller in diameter than the initial aluminum. Upon ignition at the propellant burning surface, it is hypothesized that exothermic, gas-producing reactions of aluminum with PTFE within these particles can cause them to breakup into smaller, faster burning particles. In a propellant, replacement of spherical aluminum with similarly sized Al/PTFE (70/30 wt.%) composite particles can reduce the coarse product agglomerate diameter by ~66% [22]. Though PTFE inclusion is effective at reducing agglomeration, the mechanism responsible for agglomerate size reduction is not entirely clear. It is possible heat generation from exothermic aluminum-PTFE reaction shortens aluminum particle residence time at the burning surface, decreasing chances of particle coalescence. Alternately, it is possible that gas produced from both PTFE decomposition and from aluminum fluoride sublimation causes the particles to break apart.

The individual significance of these two mechanisms in agglomerate size reduction and aluminum combustion enhancement might be determined through developing and assessing inclusion materials that result in (1) substantial gas generation accompanied by little heat release or (2) heat release without gas production. Efforts addressing the latter [21] have shown heat release alone decreases agglomeration but can also significantly reduce theoretical specific impulse. However, the sole benefits of gas production remain unknown. The question remains for inclusion modified composite particles: Can inclusion outgassing alone fragment aluminum and reduce agglomerate size?

The objective of this work is to determine if and how the mechanism of inclusion outgassing can lead to agglomeration reduction within a composite solid propellant. To achieve this goal, the effects of gas production are isolated from heat generation through the choice of low density polyethylene (LDPE) as a weakly exothermic, high gas production inclusion. Low-level (10 wt.%) inclusion modified aluminum particles are manufactured and used in a composite solid propellant to determine the effect on aluminum ignition and agglomeration. Results are compared with the previous work using 10 wt.% PTFE inclusion to understand the individual contribution of gas production. The effects of particle geometry and size on propellant density, theoretical propellant performance, burning rate, metal particle ignition, agglomeration, and metal combustion efficiency are all measured in order to determine how inclusion outgassing can alter propellant agglomeration.

2. Experimental

Thermochemical equilibrium calculations were performed on propellant, Al/polymer, and neat polymers using the Cheetah 6.0 equilibrium code [23] using the JCZS product library and JCZ3 gas equation of state. Equilibrium calculations performed on neat propellants were conducted at 0.101 MPa. For Al/polymer (90/10 wt.%) mixtures, the adiabatic flame temperature and amount of gas produced were computed at 6.9 MPa pressure. For propellant calculations, aluminum was replaced with up to 10 wt.% LDPE inclusion (1.5% propellant weight) in a composite propellant containing 71 wt.% ammonium perchlorate (AP), 14 wt.% hydroxy-terminated polybutadiene (HTPB), and 15 wt.% of either aluminum or Al/LDPE. A chamber pressure of 6.9 MPa and ideal expansion to equilibrium products at 0.101 MPa was assumed.

Five-gram batches of Al/LDPE composite particles were produced from fuel-rich mixtures of 90 wt.% aluminum (<45 μm, 99.5%, Atlantic Equipment Engineers) and 10 wt.% LDPE (500 μm, Alfa Aesar) via mechanical activation in a SPEX 8000D mill. Neat powders were continuously milled for four hours in an argon-filled (99.999%, Airgas) 50 mL steel vial (SPEX SamplePrep 8007) using 10 mm hardened steel media (Grade 1000, Frantz Manufacturing) and a charge ratio of 10. Milled, materials were processed in an argon environment and stored in hexane prior to incorporation in propellant.

Prior to use in a propellant formulation, Al/LDPE composite powders were dry sieved to between 25 and 75 μm, and their size, morphology, and thermal behavior were determined. The size distributions of the sieved MA composite powder were verified using a Malvern Mastersizer 2000 with Hydro 2000 μP dispersion unit and isopropyl alcohol as the medium. These size measurements were compared to measured distributions of similar spherical, flake, and Al/PTFE composite particles that were tested in propellants in previous work [22]. The thermal behavior of 1.5–3 mg samples of sieved powders as well as nanoaluminum (Novacentrix 80 nm) was determined by simultaneous DSC/TGA (TA Instruments Q600) over a temperature range of 100–800 °C using a 20 °C/min heating rate and 100 mL/min flow of 20/80 vol.% O2/Ar gas.

Propellant was manufactured using procedures described elsewhere [22]. Briefly, propellant consisted of 14 wt.% of a HTPB binder (cured with isophorone disocyanate, 8.3 wt.%), 71 wt.% Al (80 wt.% coarse 200 μm and 20 wt.% fine 20 μm, ATK), and 15 wt.% of sieved Al/LDPE 90/10 wt.% composite particles. The propellant was mixed in a 30 g batch for 20 min in a 250 mL container (McMaster-Carr 4290ST25) using a LabRam (Resodyn) vibratory mixer at 90% intensity. Propellant was deaerated for 15 min at <35 mbar prior to being packed into 5.8 mm diameter, ~6 cm long cylindrical strand molds and cured in air at 60 °C for approximately seven days. After curing, the density of the propellant was calculated using Archimedes principle based on the mass of an approximately one-gram piece of propellant measured both unsubmerged and submerged in a bath of anhydrous isopropyl alcohol. The
density of Al/LDPE particle containing propellant is 1.75 g/cm$^3$ (92.2% TMD), which is comparable to the densities of reference aluminumized propellants manufactured in previous work [22].

The ignition of aluminum particles at the propellant burning surface was observed at 1 atm using previously described procedures [22]. The propellant burning surface was observed using a high speed video camera (Vision Research, Phantom v7.3) with a long distance microscopic optic (Infinity Photo-Optical, K2 lens) at 11,000–20,000 frames/s using a focused, 1000 W Xenon arc lamp source (Newport Corp. #66921) for illumination. Propellant agglomerates were collected using the inert gas combustion vessel and the device shown in Fig. 1 and described in Ref. [22]. Briefly, a 23 mm tall propellant strand was ignited using an electrically heated, 24-gauge nickel–chromium wire. Once the propellant strand burns to a prescribed height, a 10 mW helium-neon laser beam (initially obstructed by the propellant strand) passes across the propellant burning surface and onto a photodiode detector on the other side of the combustion vessel. This simultaneously triggers the video recording of the combustion event (Vision Research, Phantom Miro eX4, 100 frames/s), as well as the reversal of the voltage polarity to the DC motor. The motor then sweeps a pendulum with an attached borosilicate quench disc (McMaster-Carr 8477K11) past the surface of the burning propellant at a velocity of ~7 m/s and a height of 2–6 mm above the burning surface. During this process, condensed products from propellant combustion are quenched on the surface of the borosilicate disc, which then moves to the other side of the combustion vessel where it is protected from the combustion product flow for the remainder of the experiment. The advantages and disadvantages of this quench disc technique compared to other agglomerate capture methods are discussed elsewhere [22].

Table 1
Properties of polymer inclusion materials and aluminum/polymer reactions.

<table>
<thead>
<tr>
<th>Inclusion material</th>
<th>Monomer formula</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$AH_f$ (kJ/mol)</th>
<th>$T_{\text{decomp}}$ (°C)$^a$</th>
<th>Main polymer decomposition products$^b$</th>
<th>$T_{\text{flame}, 68 \text{ atm}}$ (°C)$^b$</th>
<th>Gas production, 68 atm, $T_{\text{flame}}$ (mol/kg reactant)$^b$</th>
<th>Main reaction products$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>C$_2$H$_4$</td>
<td>0.93</td>
<td>–51.2 [33]</td>
<td>217</td>
<td>CH$_4$, C</td>
<td>305</td>
<td>6.99</td>
<td>Al, H$_2$, Al$_4$C$_3$</td>
</tr>
<tr>
<td>PTFE</td>
<td>C$_2$F$_4$</td>
<td>2.2</td>
<td>–809 [34]</td>
<td>473</td>
<td>CF$_4$, C</td>
<td>1150</td>
<td>0.00</td>
<td>Al, AlF$_3$, Al$_4$C$_3$</td>
</tr>
</tbody>
</table>

$^a$ Decomposition onset temperature measured from DSC/TGA in O$_2$/Ar (20/80 vol.%) at 20 °C/min.

$^b$ Calculated from Cheetah equilibrium code [23].

Fig. 1. Diagram of propellant combustion experiment (left), detail showing agglomerate quench device (center), and still frame showing actuation and agglomerate capture (right). Ref. [22].

Fig. 2. Electron micrograph of as-milled Al/LDPE 90/10 wt.% composite particles.

Upon completion of strand combustion, the borosilicate quench disc was extracted from the experiment and quenched agglomerates were analyzed. Surface images were taken using a FEI Quanta 3D–FEG scanning electron microscope (SEM). Agglomerate product size was determined by direct measurement (sample size of 100 agglomerates) similar to Ref. [11]. Agglomerate product phase and composition were also determined using electron dispersive spectroscopy (EDS, Oxford INCA Xstream–2 silicon drift detector) and X-ray diffraction (XRD, Bruker D8 powder diffractometer, 2°/min scan rate).
3. Results and discussion

It is clear from neat polymer properties and their reactivity with aluminum (Table 1) that LDPE is an excellent candidate inclusion material with which to study the mechanism of gas-induced particle breakup (or microexplosions). While LDPE decomposes at a lower temperature (217 °C) than PTFE (473 °C), its decomposition yields fuel products (methane and carbon) rather than strong oxidizing species (carbon tetrafluoride, CF₄) such as for PTFE. As expected, decomposition species have a significant effect on both Al/polymer (90/10 wt.%) exothermicity (adiabatic flame temperature) as well as particle gas production. The adiabatic flame temperature of LDPE inclusion modified particles (Al/LDPE 90/10 wt.%) is low (305 °C) compared to that of PTFE inclusion modified particles (Al/PTFE 90/10 wt.%, 1150 °C). At 10 wt.% inclusion level, LDPE results in 6.99 mol/g gas generation, while the adiabatic flame temperature of Al/PTFE is insufficient to generate any gaseous products (AlF₃ sublimation occurs at 1280 °C (1 atm) and generates 1.33 mol/kg gas). As such, LDPE is amenable to use in the study of inclusion outgassing as an agglomeration reduction mechanism.

Mechanically activated Al/LDPE particles, shown in Fig. 2, are packed agglomerates of small aluminum flakes. Flakes comprising the particles vary in size from ~0.5 to 5 µm in size and are less than ~0.5 µm thick. From previous study of the effects of the mechanical activation process in the Al/PTFE aluminum/polymer system [24], it is expected that in MA of Al/LDPE, the oxide coating on the exterior of neat aluminum particles is displaced and aluminum flakes are coated to some extent with LDPE, which can lead to a lower oxide content in the milled particles. The size distribution of sieved Al/LDPE composite particles is similar to sieved spherical aluminum, flake aluminum, and Al/PTFE particles of similar sizes that have been studied elsewhere [22]. Particle size distributions, obtained by laser scattering, are shown in Fig. 3 and show Al/LDPE, Al/PTFE, flake aluminum, and spherical aluminum have comparable size distributions and average particle sizes of 47.5, 31.2, 30.6, and 43.3 µm, respectively. While the size distributions for spherical aluminum particles are lognormal, the distributions of Al/LDPE, Al/PTFE, and flake aluminum are skewed as a result of non-spherical particle geometry.

Simultaneous DSC/TGA oxidation experiments on Al/LDPE composite particles and reference aluminum powders (Fig. 4) indicate that LDPE inclusion results in significant improvement in particle oxidation characteristics. In heating of Al/LDPE particles, we first observe exothermic decomposition and reaction of LDPE with oxygen starting at ~220 °C and occurring over a broad temperature range. This is consistent with DSC/TGA of neat LDPE and similar data reported elsewhere [25]. Decomposition of LDPE ceases at ~550 °C, corresponding to a 10% loss in weight. Shortly thereafter, oxidation of aluminum onsets as a result of exothermic aluminum oxide phase transformation and densification from amorphous to γ-Al₂O₃ [26]. Oxidation slows after ~630 °C due to growth of a protective γ-Al₂O₃ oxide shell [27]. The enhancements in oxidation that result from LDPE inclusion are apparent from the observed total weight gain that occurs during DSC/TGA heating. While spherical and flake aluminum gain 5% and 20% weight, respectively...
in heating to 800 °C, Al/LDPE results in a 45% weight gain, which is surpassed only by nAl (60% weight gain).

Thermochemical equilibrium calculations were also used to assess the thermodynamics of aluminum combustion in a composite propellant. Considering propellant flame temperatures, it is apparent that addition of LDPE (Al/LDPE 90/10 wt.%) at the cost of aluminum reduces performance slightly. At 6.9 MPa pressure, the adiabatic flame temperature decreases linearly with LDPE addition by about 150 °C to ~2880 °C (10 wt.% inclusion). This reduction in flame temperature along with an increase in gaseous exhaust species molecular weight leads to a 1.0% (2.7 s) decrease in the predicted specific impulse, from 262.7 to 260.0 s (Fig. 5). In comparison, addition of 10 wt.% PTFE decreases propellant adiabatic flame temperature by 60 °C and decreases predicted specific impulse by 0.8% (2.1 s).

Supplemental video and images of composite solid propellant deflagrating at 1 atm pressure (Figs. 6 and 7) show the pronounced effect 10 wt.% LDPE inclusion modification has on aluminum particle ignition and combustion. In previous work [22], the ignition and agglomeration effects of geometry (spherical vs. flake) were discussed. Briefly, these results indicated that though flake particle geometry promotes ignition at the surface, it also increases agglomeration due to longer particle residence time (Fig. 6). Though Al/LDPE particles are mostly comprised of agglomerated flakes, Fig. 6 and the supplemental video show that replacement of neat aluminum with Al/LDPE particles results in prompt particle ignition at the burning surface and overall smaller burning particles. This is similar to the observed effects of aluminum replacement with Al/PTFE particles.

Like PTFE, LDPE inclusion results in particle ignition nearer the burning surface, though it does so by a mechanism much different than the mechanism believed to be responsible for enhanced ignition of Al/PTFE particles. Aluminum/PTFE particle ignition is hypothesized to occur from decomposition of PTFE inclusions to gaseous oxidizing species, which spread aluminum particles apart through exothermic reaction with both aluminum and aluminum oxide. Conversely, LDPE inclusion heating results in decomposition to fuel species that are not expected to strongly react with aluminum. It might be possible that these species may help expose additional aluminum surface through spreading and breakup of particles during decomposition. However, ignition requires the diffusion of AP oxidizing species to aluminum particle surfaces. Reactivity of these particles with propellant oxidizing species may,
however, be improved through exposure of unoxidized aluminum surfaces initially protected by the LDPE inclusion material. Regardless of the differences in ignition mechanisms, Fig. 6 and the supplemental video show that ignition of Al/LDPE inclusion modified particles occurs at the burning surface and that resulting agglomerates are much smaller than flake aluminized agglomerates. In comparison to propellants containing Al/PTFE inclusion modified particles, one apparent difference is that LDPE inclusion produces less product smoke than PTFE. This could be in part due to the LDPE combustion in a propellant forming non-condensable, gaseous species (H$_2$O, CO and CO$_2$ as predicted by equilibrium code [23]) unlike PTFE, which forms AlF$_3$ and other condensable aluminum oxy-fluorides [22].

Improvements in agglomeration observed at 0.1 MPa pressure are also apparent at motor pressure. At 6.9 MPa pressure, agglomerates were captured at a distance of $\sim$2–6 mm from the propellant burning surface using the quench disc technique described in Ref. [22] and shown in Fig. 1. High magnification SEM images

Fig. 8. High magnification electron micrograph of quenched agglomerates from Al/LDPE 90/10 wt.% inclusion modified propellant combustion at 6.9 MPa. Left: coarse agglomerate covered with fine agglomerates. Right: 10,000× magnification detail of surface showing nanoscale cracks.

Fig. 9. Electron micrographs of quenched coarse fraction agglomerates from 6.9 MPa combustion of propellant containing 25–75 µm particles of spherical aluminum, flake aluminum, or Al/PTFE 90/10 wt.% particles (Ref. [22]) compared to agglomerates quenched from propellant containing Al/LDPE 90/10 wt.% composite particles.
of quenched agglomerates, as captured on the disc surface, are shown in Fig. 8a. The condensed phase products contain both a coarse and fine (<3 μm) fraction, and the surfaces of the coarse particles (Fig. 8b) contain nanoscale cracks. The coarse fraction of condensed products results in the most detrimental two-phase flow loss, and as such is of particular interest here. Lower magnification SEM images of agglomerate products (Fig. 9) show coarse agglomerates produced from propellant combustion at 6.9 MPa. Previous work [22] examined the effects of aluminum particle geometry and diameter on the coarse fraction agglomerate size. Briefly, results indicated that flake geometries promote agglomeration. In replacement of aluminum with Al/PTFE 90/10 wt.% particles, combustion products were noticeably smaller and significantly more fine fraction “smoke” particles were present. Similarly, products from Al/LDPE 90/10 wt.% propellant combustion contain coarse agglomerates that are appreciably smaller than those from spherical or flake aluminized propellant. However, products from propellants containing Al/LDPE contain fewer fine fraction particles than those from propellants with Al/PTFE particles. Sizing of these agglomerates (Fig. 10) indicates average coarse agglomerate sizes of 75.8 and 125 μm, respectively, for spherical and flake aluminized propellants. Replacement of aluminum with Al/PTFE 90/10 wt.% particles has been shown to reduce average coarse agglomerate size to 54.7 μm [22]. In comparison, Al/LDPE 90/10 wt.% particle containing propellant produces on average 29.0 μm diameter agglomerates which are ~60% smaller (a 94% decrease in agglomerate volume) than spherical aluminized propellant products. This evidence suggests that highly exothermic reaction of inclusion material with aluminum is not a prerequisite to reduction in coarse agglomerate size. Low reactivity, high gas-producing inclusion materials (such as LDPE) might be more effective at reducing coarse agglomerate size, as they may delay aluminum melting until particle fragments have been dispersed and are less likely to coalesce.

While direct observation of propellant combustion products shows coarse agglomerate size is reduced, chemical analysis of products suggests low level LDPE inclusion modification also enhances aluminum combustion in vicinity of the propellant surface. X-ray diffraction (Fig. 11) shows Al/LDPE 90/10 wt.% propellant products are comprised of a number of different aluminum oxide phases. Of these phases, α-Al2O3 is particularly prominent. Qualitative comparison of peak ratio heights for Al/LDPE 90/10 wt.% and spherical aluminized propellant products (Fig. 11) shows that Al/LDPE particles result in a stronger α-phase Al2O3 formation, which is indicative of a higher temperature near the propellant surface. This also suggests a greater heat liberation due to formation of a lower energy state, α-phase, alumina [26,28]. Perhaps the most notable indication that Al/LDPE 90/10 wt.% particles produce a higher flame temperature and greater heat release near the burning surface is the presence of unreacted, crystalline aluminum and trace AP in products quenched from spherical aluminized propellant.

As is expected, inclusion modified Al/LDPE particles have an effect on composite propellant linear burning rate. Shown in Fig. 12, below 6.9 MPa pressure, the effect of Al/LDPE particles on propellant burning rate is similar to that of flake aluminum studied previously [22]. Replacing spherical aluminum particles with Al/LDPE particles increases the burning rate pre-exponent from 0.49 to 0.57 while only slightly changing pressure exponent from 0.36 to 0.37. This is also similar to the effect of replacing composite propellant micron-scale spherical aluminum with nanoscale aluminum that has been observed by others [29]. However, Al/LDPE...
90/10 wt.% particles result in a burning rate slope break at 6.9 MPa, above which the pressure exponent is 0.10 and burning rate is only weakly sensitive to pressure. Previous studies on the phenomena related to plateau burning in composite propellants have focused on effects of coarse and fine AP size [30] and binder melt-flow [31] of non-aluminized AP composite propellants. However, a recent study [32] of the addition of nanoscale aluminum at the expense of coarse AP shows nano-Al can intensify plateau burning effects. While consistent with the effects of nano-Al addition, the mechanism responsible for plateau combustion in propellants containing Al/LDPE composite particles remains unknown.

4. Conclusions

This work shows that through use of 10 wt.% LDPE inclusion within aluminum (1.5% of propellant weight), it is possible to significantly reduce coarse agglomerate size. The near-surface capture technique used shows inclusion modified particles decrease coarse agglomerate size from 75.8 \( \mu \text{m} \) (spherical aluminum) to 29.0 \( \mu \text{m} \) (Al/LDPE 90/10 wt.% particles). Though equilibrium calculations indicate 10 wt.% LDPE inclusion reduces predicted specific impulse by 1.0% from 262.7 to 260.0 \( \text{g/s} \), it is possible that in a motor configuration, the reduction in two-phase flow loss caused by LDPE inclusion will exceed this performance reduction, resulting in a net performance increase. Further, this work shows that use of LDPE inclusion modified particles enhances aluminum combustion near the propellant surface, leading to more complete aluminum oxidation to the stable, \( \alpha \)-alumina phase. This also suggests that LDPE inclusion results in higher temperatures near the propellant burning surface. Inclusion modified Al/LDPE particles result in an increase in burning rate pre-exponent from 0.49 (spherical aluminum) to 0.57 at pressures below 6.9 MPa, but cause plateau pressure dependence (an exponent of 0.10) at pressures above 6.9 MPa. While the mechanism responsible for this is unknown, high-pressure plateau combustion can reduce motor safety margins and simplify higher-pressure operation.

In comparison to previous results using PTFE as the inclusion material, this work suggests that in order for coarse agglomerate size to be reduced, inclusion outgassing (with little heat generation) might be sufficient and highly exothermic aluminum/inclusion reactions may not be necessary for agglomeration reduction. This is significant, as low exothermicity, gas-producing inclusions that result in increased theoretical specific impulse can be considered for further performance improvements. Due to their low exothermicity, such inclusion materials could also improve the safety of the mechanical activation process. For example, the safety considerations pertinent to Al/PTFE particle manufacture (ignition during production) are not applicable to Al/LDPE, making larger scale manufacturing readily achievable. This work demonstrates LDPE inclusion as a safe, low cost, scalable technique to reduce composite propellant agglomeration, enhance aluminum combustion near the propellant surface, and produce high-pressure plateau burning rate pressure dependence.

Current and future efforts are focused on other inclusion materials that result in a net increase in theoretical specific impulse performance as well as study of inclusion modified particle ignition at various heating rates and in different environments. Future efforts will also investigate the mechanism through which LDPE inclusion leads to high-pressure plateau combustion.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.combustflame.2014.08.013.

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