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Development of flexible, free-standing, thin films for additive manufacturing and localized energy generation

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Development of flexible, free-standing, thin films for additive manufacturing and localized energy generation

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Film energetics are becoming increasingly popular because a variety of technologies are driving a need for localized energy generation in a stable, safe and flexible form. Aluminum (Al) and molybdenum trioxide (MoO₃) composites were mixed into a silicon binder and extruded using a blade casting technique to form flexible free-standing films ideal for localized energy generation. Since this material can be extruded onto a surface it is well suited to additive manufacturing applications. This study examines the influence of 0-35% by mass potassium perchlorate (KClO₄) additive on the combustion behavior of these energetic films. Without KClO₄ the film exhibits thermal instabilities that produce unsteady energy propagation upon reaction. All films were cast at a thickness of 1 mm with constant volume percent solids to ensure consistent rheological properties. The films were ignited and flame propagation was measured. The results show that as the mass percent KClO₄ increased, the flame speed increased and peaked at 0.43 cm/s and 30 wt% KClO₄. Thermochemical equilibrium simulations show that the heat of combustion increases with increasing KClO₄ concentration up to a maximum at 20 wt% when the heat of combustion plateaus, indicating that the increased chemical energy liberated by the additional KClO₄ promotes stable energy propagation. Differential scanning calorimeter and thermogravimetric analysis show that the silicone binder participates as a fuel and reacts with KClO₄ adding energy to the reaction and promoting propagation. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4928570>]

I. INTRODUCTION

Thin film energetic composites are a growing area of research because of their great potential at providing localized power generation in miniaturized applications. One synthesis approach combines fuel and oxidizer powders with a binder and solvent system and blade casts the mixture into a film. This technique has been utilized previously in the manufacture of capacitors and batteries¹⁻³ as well as for rapid prototype fabrication of laminated ceramic components.^{4,5} The first reporting of blade casting of an energetic material was for thermal battery applications and utilized magnesium (Mg) and manganese dioxide (MnO₂) as the energetic composite combined with various binder-solvent systems.⁶ Meeks et al. showed that polyvinylidene fluoride (PVDF) and n-methylpyrrolidone (NMP) were an effective fluoropolymer binder and organic solvent combination because they enabled greater homogeneity (i.e., less settling and segregation of particles) and lead to improved combustion.⁶ They synthesized 60 x 6 mm and 100 micron thick films that were deposited and adhered to substrates. The films produced calorific output on the order of 4 kJ/g and energy propagation on the order of 0.14 m/s, suitable for thermal battery applications.

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TABLE I. Combustion property data reported by Fischer *et al.*¹⁵ Adiabatic flame temperature calculations assume phase changes. Mg + MnO₂ has been used previously for thin film thermites.⁶ Al + MoO₃ is the proposed formulation investigated in this study.

Composition	ΔH_c (J/g)	g moles of gas per 100 g	T_{af} (K)
Mg + MnO ₂	5531.3	0.7378	3271
Al + MoO ₃	4702.8	0.2425	3253

This study expands on the current understanding for synthesizing blade cast energetic films by preparing thicker films (i.e., a few mm thick) that can be removed from the substrate and behave as flexible free-standing energetic films. An advantage to this synthesis method is that the final film is an easy to handle, consolidated means for providing localized power generation. Also, the fundamental understanding for preparing these films is a first step toward extrusion type additive manufacturing techniques for 3D printing of energetic materials. This type of manufacturing for the production of energetic materials could allow for rapid prototyping with reduced handling thereby improving the safety of material synthesis.

For this study aluminum (Al) fuel particles were combined with molybdenum trioxide (MoO₃) particles and used as the base thermite. This is a commonly studied thermite system^{7–10} and has even found applications as a primer replacing lead styphnate.^{11–14} Because this study expands on the blade casting method presented by Meeks *et al.*⁶ it is constructive to compare the base thermites used in both studies. Table I compares heat of combustion (ΔH_c), gas generation (g) and adiabatic flame temperature (T_{af}) for both the Mg + MnO₂ and Al + MoO₃ stoichiometric reactions.¹⁵ The low gas generating nature of Al + MoO₃ is an advantage given the non-porous nature of the film. Specifically, low porosity limits the advection of convective energy such that low gas generation may promote diffusive energy propagation and overall increase the rate of energy released. While Al + MoO₃ has a lower ΔH_c than Mg + MnO₂, T_{af} for both reactions are comparable indicating that thermal energy liberated from the chemical reaction combined with lower gas production may promote energy propagation in the film comprised of Al + MoO₃ compared with Mg + MnO₂.

An additional oxidizer, potassium perchlorate (KClO₄), was also included to facilitate oxygen transfer to the aluminum and selected for the abundance of available oxygen. Farley *et al.*¹⁶ examined the combustion properties of Al + KClO₄ and found this mixture to be relatively non-gas generating compared to thermites such as Al + I₂O₅,¹⁶ Al + MoO₃,^{8,17} and Al + CuO.⁷ Because these high bulk density films have limited porosity, gas generating oxidizers may inhibit the diffusion of energy through the film and hinder flame speed. This makes KClO₄ a desirable oxidizer¹⁶ because of its high oxygen content and its low gas generation. Farley *et al.*⁶ also showed that Al + KClO₄ produced orders of magnitude slower flame speeds in comparison to Al with other solid oxidizers (e.g., silver iodate, calcium iodate and iodine pentoxide) indicating that Al + KClO₄ is not particularly reactive.

The binder solvent system used with this ternary composite was silicone and xylene. Silicone was selected to eliminate fluorine from the binder system in an effort to reduce the corrosive properties of the combusting mixture.^{18–20} Silicone can be dissolved in xylene, such that the solvent system is selected based on compatibility with the binder.⁶

The objectives of this study were to synthesize flexible free-standing energetic films using blade casting and to assess the influence of KClO₄ concentration on energy propagation of the resulting film. Energy propagation was evaluated from flame speed measurements that provided an empirical quantification of energy release rates available from the reactions.^{7–9,16,21–23} These experiments were complemented by thermal equilibrium simulations performed using REAL code software to calculate combustion properties. Additional experiments were performed to characterize the reaction kinetics using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The combined analysis, flame speed and DSC/TGA, enabled an understanding of not only the energy propagation in these materials but also the equilibrium reaction kinetics.

TABLE II. Material descriptions and supplier information.

Material	Supplier	Characteristic Particle Length (μm)
Al	Nova Centrix (Austin, Tx)	0.080
MoO ₃	Alfa Aesar (Ward Hill, Ma)	14.0
KClO ₄	Sigma Aldrich (St. Louis, Mo)	151.0
Mold Max 30 Silicone	Smooth-On (Easton, Pa)	N/A
Xylene	Macron Fine Chemicals (Center Valley, PA)	N/A

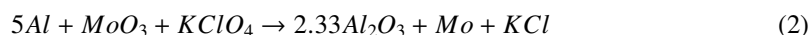
II. EXPERIMENTAL SETUP

A. Materials

The films were synthesized using a combination of an energetic composite, an additive, and a binder-solvent system. Aluminum (Al) and molybdenum trioxide (MoO₃) were the energetic composite for all films and mixed at a stoichiometric ratio. The reaction for this base energetic composite is shown in Eq. (1).



Potassium perchlorate (KClO₄) was added in varying mass percentages, 0-35wt%, which caused the global reaction to become increasingly fuel lean.²⁴ The global reaction is shown in Eq. (2).



The binder-solvent system included silicone and xylene. The mass of silicone was held constant for all films, while the mass of xylene was increased to ensure all films were cast at 55% solids concentration by volume. Table II shows the name, supplier, morphology of the particles and applicable particle size for all the materials used in the films. With the exception of KClO₄ the mass of all other components were held constant.

B. Film Synthesis

The base energetic reaction consisted of 670 mg of Al and 1790 mg of MoO₃. Table III shows the mass of KClO₄ corresponding to the percent added to the powder components of the base reaction. The mass of KClO₄ for each percent was found using only the mass of the Al, MoO₃, and silicone binder. The solvent was excluded from the mass percent calculation due to the film being dried before testing. These components are then sealed in a mixing vessel while the binder-solvent system was prepared. The silicone binder is a two part tin-cured silicone. The total mass of binder used in each film was 3632 mg. The binder was mixed by hand with an appropriate mass of xylene (Table III) to maintain a constant solids concentration. The binder solvent system was added to the powder in the mixing vessel and components were mixed using a centripetal planetary mixer (Thinky) at 1600 RPM for 90 seconds. Total batch masses varied from 7503 mg for the 0% KClO₄ film to 12041 mg for the 35% KClO₄ film.

TABLE III. Mass of KClO₄ and Xylene corresponding to mass percent KClO₄.

KClO ₄ wt. %	Mass KClO ₄ (mg)	Mass Xylene (mg)
0%	0.00	1410
5%	304	1753
10%	609	2097
15%	914	2440
20%	1218	2784
25%	1523	3127
30%	1828	3471
35%	2132	3814

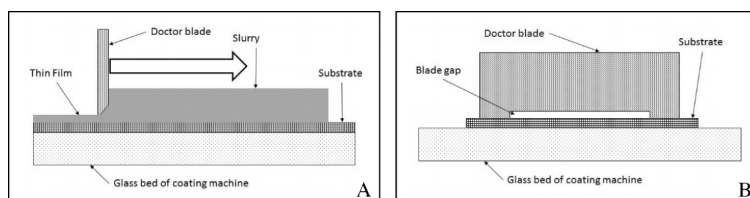


FIG. 1. Schematics showing film preparation setup. A. Side view of doctor blade being drawn across slurry to make thin film. B. Frontal view of doctor blade.

Once mixing is complete, the slurry is placed in a vacuum chamber and subjected to 50 kPa vacuum to de-aerate the slurry before loading onto a doctor blade apparatus, schematically shown in Figure 1. The doctor blade is used to create a uniform thin film by drawing the blade over a slurry to produce a constant 1 mm thick film on a substrate, which is shown in Figure 1(A). The thickness of the film is equal to the gap height of the blade shown in Figure 1(B). All films were coated onto stainless steel foil substrates that were 50 microns thick. The coatings were then placed in an oven at 60°C for 24 hours to evaporate the solvent. After drying, the coatings were cooled at room temperature in a fume hood for 24 hours. The free standing film is photographed in Figure 2. The film was cut into 6 x 50 mm strips, 1 mm thickness using scissors for combustion experiments.

C. Energy Propagation

To establish repeatability, four samples of each composition were examined and flame speeds were measured. A glass slide with the sample strip attached was placed on a steel block housed in a combustion chamber with viewing windows. The sample was aligned with the camera perpendicular to the direction of flame propagation. The film was ignited with a butane flame and the energy propagation was recorded at 250 frames per second at a resolution of 800 x 480 pixels using a Vision Research Phantom VII high speed camera. The videos were converted to a series of still images and were processed to find the horizontal position of the leading edge of the flame using National Instruments Vision software. The reported flame speeds represent the average of four samples. The uncertainty reported corresponds to the standard deviation of the four samples measured, which is the largest source of uncertainty in the experiments.

D. Thermal Equilibrium Studies

REAL code (Timtec L.L.C.), a thermal equilibrium software model, was used to calculate theoretical heat of combustion of the global reaction in Eq. (2). These simulations were performed assuming a constant volume of 0.01 m³/kg and internal energy equal to zero.

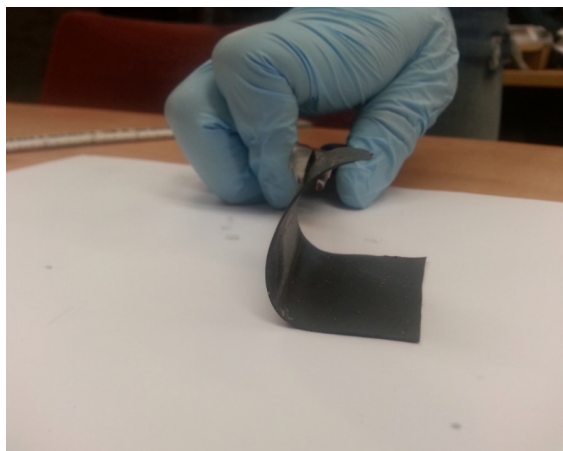


FIG. 2. Photograph showing flexible free standing energetic thin film.

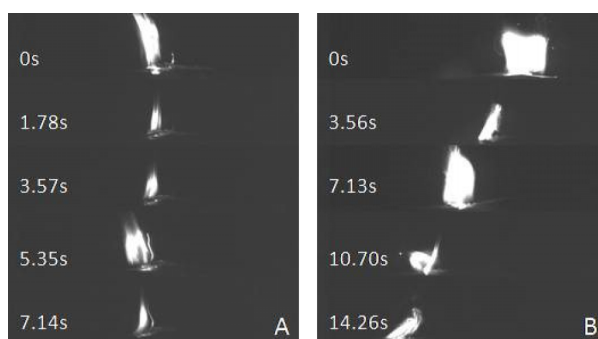


FIG. 3. A. Thermal instabilities illustrated by unsteady energy propagation from film containing 0 wt% KClO_4 concentration. B. Steady energy propagation observed for films with 30 wt % KClO_4 concentration.

A Netzsch STA 449 DSC and TGA was used to measure the heat flow as a function of temperature and time. For the DSC analysis, a 10 mg sample of each film was loaded into an alumina crucible with no lid and placed in the diagnostic. Samples were heated to 900°C in an air environment at 10K/min (KPM). The sample is compared to an empty reference sample in order to gather energy and mass change data during the heating process. The temperature where the slope of the DSC graph changes is defined as the onset temperature. Sintering can occur during heating and melting, ultimately affecting heat transfer in the STA measuring head. To establish consistency, repeatability and minimize artifact alterations of results, three experiments were performed for each sample. Temperature calibrations for the instrument were performed using melting of a set of metal standards resulting in a temperature accuracy of $\pm 1^\circ\text{C}$.

III. RESULTS AND DISCUSSION

Figure 3 shows representative still frame images of reaction propagation of two films that vary by KClO_4 concentration. Figure 3(A) shows the unsteady propagation of a 0 wt% KClO_4 sample compared with Figure 3(B) that shows steady state propagation of a 30 wt% KClO_4 sample. In Figure 3(A) the flame appears to spiral and exhibits oscillating behavior seen at the leading edge of the flame. This instability has been observed in previous combustion studies of solid energetic composites.^{25,26} Munir and Anselmi-Tamburini attribute this behavior to thermal instabilities that can manifest from perturbation of variables that reduce the flame temperature and reaction energy.²⁵ Malchi et al.²⁶ observed thermal instabilities with $\text{Al} + \text{CuO}$ and $\text{Al} + \text{MoO}_3$ propagation when a diluent was added at high concentrations. The diluent in Malchi et al.²⁶ was alumina and did not participate in the reaction but acted as a thermal heat sink. Similarly, in this study the silicone binder may act as a heat sink in the low KClO_4 concentration samples. To investigate this possibility, DSC analyses were performed to assess the exothermic behavior of silicone binder alone and combined with each individual reactant. Figure 4 shows the silicone binder exhibits exothermic behavior with

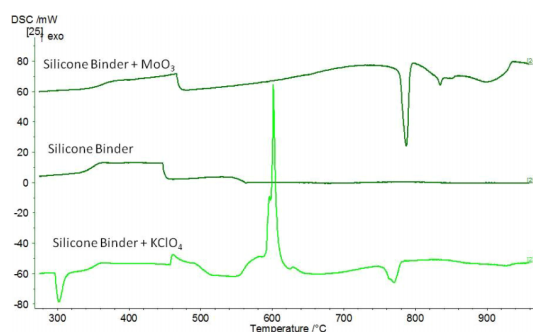
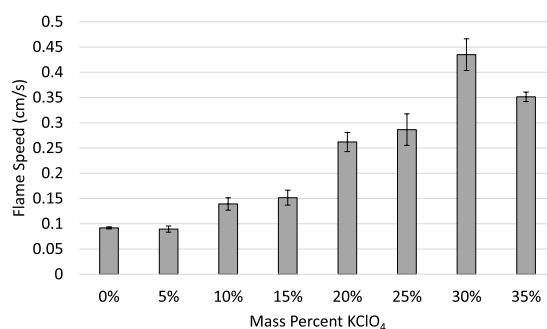


FIG. 4. Heat flow results from DSC analysis showing silicone binder alone, mixed with KClO_4 and MoO_3 ; experiments performed in air at a heat rate of 10 KPM.

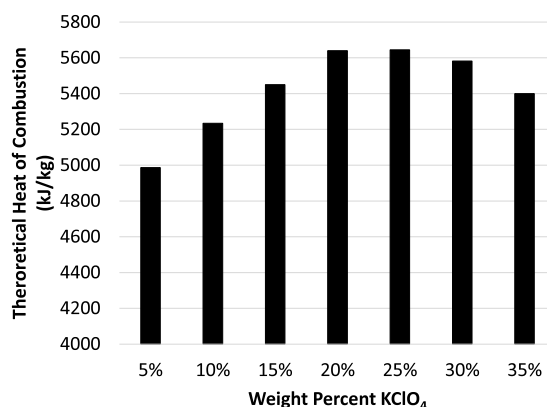
FIG. 5. Average flame speed as a function of mass percent KClO₄ concentration.

KClO₄ starting at 550 °C but not with the other reactants. The lack of reactivity with the other reactants gives strong evidence that the silicone binder acts as a thermal sink in the reactions with low concentrations of KClO₄.

In Figure 3(B) the increased KClO₄ concentration promotes steady propagation with no observed thermal instabilities. Figure 4 suggests that added KClO₄ may react with the silicone binder such that the binder provides chemical energy to the overall reaction to overcome the thermal instabilities observed at lower KClO₄ concentrations. The reaction between silicone binder and KClO₄ has been previously documented by Williams *et al.*²⁷ They found the reaction to be highly gas generating and potentially useful as inflators for restraint systems.²⁷ However, the appearance of the flame is not consistent among sequential frames (Figure 3(B)) with varied flame width observed by light intensity. While the leading edge propagates forward consistently, the range of heated film illuminated shows an overall non-uniform propagation.

Figure 5 shows the average flame speeds for all compositions with the associated uncertainty. As the mass percent KClO₄ is increased the average flame speed is increased up to a maximum at 30 wt. % KClO₄ of 0.435 cm/s. The uncertainty bars demonstrate the high repeatability in energy propagation of these synthesized materials. It is noted that a film composed of Al + KClO₄ was also prepared using the same binder – solvent system. The result was that without MoO₃, the film cannot sustain self-propagation and quenches upon ignition.

The simulation results in Figure 6 show a relative ΔH_c plateau in the range of 20-30 wt. % KClO₄ concentration corresponding to roughly 5600 kJ/kg. Also noteworthy is that the gradual increase in ΔH_c (in Figure 6) correlates well with the increase in flame speed up to 20 wt% KClO₄ (Figure 5). The correlation implies the increasing trend in flame speed (Figure 5) is promoted by higher energy content of the reaction. At 20 wt. % KClO₄ the thermal instabilities in energy propagation are also no longer observed, also consistent with diffusion controlled energy propagation.^{25,26} However, for KClO₄ concentrations greater than 20%, energy liberated from the reaction is

FIG. 6. Theoretical heat of combustion for global reaction with varying KClO₄ concentration.

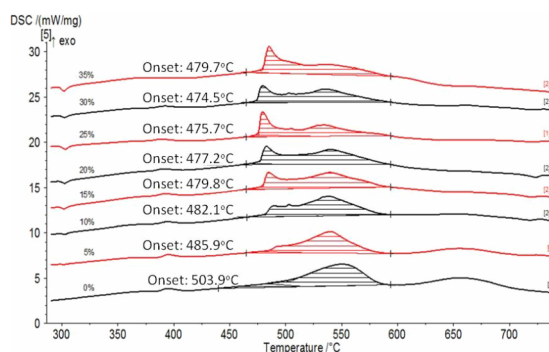


FIG. 7. Heat flow results from DSC measurements on films with varying KClO_4 concentrations in air; experiments performed at a heating rate of 10 KPM.

minimally affected by further increases in KClO_4 concentration such that further increases in energy propagation are no longer attributed to additional energy content from the reaction chemistry. These simulations do not account for silicone, but the trends in heat flow shown in Figure 6 are consistent with the flame propagation observations in Figure 3; suggesting that the silicone binder has limited participation in chemical energy liberated at low (i.e., < 20 wt. %) KClO_4 concentrations.

Figure 7 shows heat flow curves measured using the DSC for each sample analyzed in Figure 5. A dramatic shift in the exothermic reaction from 0-30 wt% KClO_4 indicates the addition of KClO_4 alters the mechanism for reaction. As the concentration of KClO_4 increases the onset reaction temperature decreases to a minimum at 30 wt. % KClO_4 (in Figure 7 from 503.9 to 474.5 °C). Since KClO_4 has a lower enthalpy of formation (-430.12 kJ/mol) than MoO_3 (-745.17 kJ/mol), less energy is required for the fuels (and in particular the silicon) to oxidize with KClO_4 compared with MoO_3 .²⁸ As KClO_4 concentration increases, the onset temperature is reduced by 24.2°C because the silicone binder onset with KClO_4 (seen in Figure 4 as 461°C) is before the onset of Al oxidation (seen in Figure 7 as 503°C). The silicone binder participating in the reaction owing to the greater oxygen content at higher KClO_4 concentrations as seen in Figure 4. The exothermic interaction between the silicone binder and KClO_4 is unique and not observed with the MoO_3 oxidizer. As KClO_4 concentration increases, participation of the silicone binder as a fuel in the overall exothermic reaction contributes added heat to stabilize energy propagation.

Figure 8 shows the mass loss curves measured with the TGA. The addition of KClO_4 introduces a multiple step mass loss, which becomes more pronounced in the higher KClO_4 concentration films. This multistep behavior may be indicative of the silicone binder reacting as a fuel. Figure 4 shows the binder onset with KClO_4 at 461°C coincident with the second mass loss step. If the heat flow trace for silicone binder in Figure 4 is examined, an exotherm is present beginning at 337°C. This exotherm corresponds to the silicone reacting with the air environment present in the DSC. This reaction correlates to the first mass loss present in the mass loss curves in Figure 7 for the films. This leads to an increasingly lean global reaction when KClO_4 is added to the films. This shift

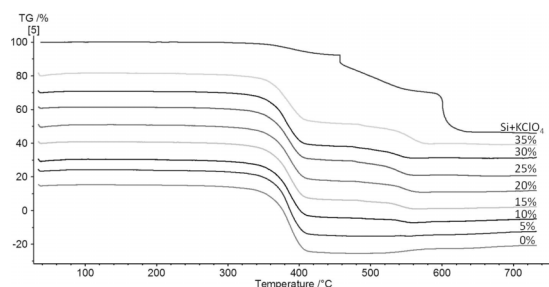


FIG. 8. Mass loss trends from TGA measurements on films with varying KClO_4 concentrations in air at a heat rate of 10 KPM. Top curve represents Si binder + KClO_4 . All other curves represent Al + MoO_3 + x% KClO_4 as indicated.

in stoichiometry may be responsible for the increase in onset temperature for the 35 wt. % KClO_4 sample. The results from analysis of equilibrium kinetics provides evidence that while the heat of combustion remains relatively unchanged between 20-30 wt. % KClO_4 , the temperature required to initiate the reaction is reduced to a minimum at 30 wt. % KClO_4 . If flame propagation is considered to be a continual series of ignition events, assuming thermal properties are not significantly changing and convective influences are negligible, then the film that requires the lowest temperature to achieve ignition should display the fastest flame speeds, as seen here. Also, lower onset temperature and more liberated heat from the silicone binder participation in the reaction facilitates more heat transfer through the film and enables stable propagation.

IV. CONCLUSIONS

We successfully synthesized flexible free standing energetic thin films using a blade casting approach and a base thermite system, binder, solvent, and additive. The base thermite consisted of aluminum, Al, and molybdenum trioxide, MoO_3 added to a silicone-xylene binder-solvent system. Varied concentrations of KClO_4 , from 0-35 wt. %, were investigated to understand the effect on the combustion properties. Films were synthesized to further examine energy propagation as a function of KClO_4 concentration. As KClO_4 concentration increased, energy propagation stabilized and increased up to a maximum of 0.435 cm/s at 30 wt. % KClO_4 . At a threshold of 20 wt. % KClO_4 , thermal instabilities were no longer observed and sustained steady propagation was achieved. Differential scanning calorimeter analysis revealed that the addition of KClO_4 promoted early reaction onset, likely caused by the KClO_4 lower heat of formation and reaction with the silicone binder. The additional heat liberated by the reaction between the KClO_4 and silicone binder facilitated stable energy propagation, while the lower onset temperature promoted flame speed. The activation of the silicone binder and KClO_4 reaction is significant because the binder acts as a fuel in the reaction, as opposed to an oxidizer. These observations will help further develop energetic thin film technology that can be used on any application requiring localized power generation. In addition to localized power generation these compositions can be used in extrusion type additive manufacturing techniques to produce energetic materials.

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