Synthesis and characterization of flexible, free-standing, energetic thin films

Billy R. Clark [a], Michelle L. Pantoya [a,*], Emily M. Hunt [c], Trent J. Kelly [c], Benton F. Allen [c], Ronald J. Heaps [b], Michael A. Daniels [b]

[a] Mechanical Engineering Department, Texas Tech University, Lubbock, TX 79409, United States
[b] Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415, United States
[c] Department of Engineering and Computer Science, West Texas A&M University, Canyon, TX 79016, United States

ABSTRACT

This study uses blade casting methods for the synthesis of flexible, free-standing energetic films. Specifically, films include aluminum (Al) and (MoO_3) powder thermites combined with potassium perchlorate ($KClO_4$) and silicone binder. In addition to this base composite, carbon fiber fabric reinforcement fabric has been incorporated to improve the structural integrity of the film. All films were cast at 1 mm thickness with constant percent solids to ensure consistent rheological properties. The films were ignited and flame propagation was recorded with a high speed camera. The results show that the energy propagation of the films increases with increasing mass percent $KClO_4$. The inclusion of carbon fiber fabric reinforcement fabric in the energetic film decreased the flame speed by 30% but maintained stable and steady energy propagation. The strengths of the films were tested to determine the effects of the carbon fiber fabric reinforcement fabric on the mechanical properties of the films. The non-reinforced film, failed upon initial loading of approximately 2.27 kg while the reinforced film maintained a load of 72.3 kg. While this method of synthesis allows manufacture of a flexible free-standing energetic film, the composition and rheology of the mixed slurry have potential as an extrusion cast energetic for additive manufacturing of energetic materials.

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1. Introduction

Powder composite energetic materials are mainly composed of a metal fuel and an oxidizer mixed to various ratios that enable tailorability toward particular applications. The numerous combinations of fuel and oxidizer reactions that are possible make these materials suitable for anything from killing harmful bacteria [1], welding [2], and under water energy generation [3,4]. Since the powder forms of these materials are not suitable for many applications, often some form of consolidation is required [3,4]. A new method to consolidate powders is presented here and advances the development of energetic slurries that can be extruded. The method effectively synthesizes a free standing flexible film that consistently produces localized energy when ignited. This method is a first step toward the development of additive manufacturing or 3-D printing of energetic materials because the slurry can be injection molded or extruded to create any desired shape.

Various methods exist for creating energetic films including magnetron sputter deposition [5], and vapor deposition [6]. Meeks et al. introduced thin film energetics using a similar blade casting method, and produced 0.1 mm thick films adhered to substrates and characterized their flame speed and heat of combustion [7]. Their magnesium and manganese oxide based films contained 0.5–7 wt.% binder which produced a film that was well adhered to the substrate and flame speeds on the order of 100 cm/s [7].

Blade casting is a cost effective and efficient means of creating large films in various thicknesses. The process involves creating a slurry that is spread over a substrate using a blade, to create a film with a prescribed thickness. This process has been used in various industries for several decades. One of the first uses was to create multilayered capacitors in the late 1940s through early 1950s [8,9]. The blade casting process also makes it possible to produce functionally gradient materials (FGM). These materials are produced by laminating multiple layers of different chemical compositions [10]. Recently this process has been used extensively in the creation of lithium based batteries [11] and also for rapid prototyping of laminated ceramic engineering components [12]. The term blade casting is often used interchangeably with tape casting, but generally tape casting produces films on the order of microns thick (i.e., tapes) while blade casting produces films on the order of millimeters thick or thicker, yet the process is similar.

In this study we focus on developing blade casting methods for the synthesis of flexible, free-standing energetic material films. Specifically,

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* Corresponding author.
E-mail address: michelle.pantoya@ttu.edu (M.L. Pantoya).

films include Al and MoO_3 powder thermites combined with $KClO_4$ to aid combustion of the Al and silicone based binder. In addition to this base composite, reinforcement fabrics have been incorporated to improve the structural integrity of the film. Specifically, carbon fiber fabrics are used for applications where high strength and low weight are desirable such as aircraft [13,14], high performance automobiles [15, 16], in addition to various other industries. While this material has been used extensively in various industries for years, the integration of these reinforcement fabrics into energetic materials has not been studied. Carbon fiber fabric is utilized in this study to determine the effect of the material on the mechanical properties and energy propagation of the films synthesized with this fabric. Adding structural integrity to an energetic film could have potential for structural energetic material applications.

2. Experimental details

2.1. Compositions

The films are synthesized using a combination of an energetic composite, an additive, and a binder system. Aluminum (Al) and molybdenum trioxide (MoO_3) powder is used as the energetic composite for all films. Potassium perchlorate ($KClO_4$) is used as the additive in varying mass percentage concentrations. The binder system includes Mold Max® 30 RTV silicone and xylene. A 12 by 12 plain weave carbon fiber fabric, supplied by APC Composites (Livermore, CA), made of medium modulus carbon strands produced from polyacrylonitrile is used as the reinforcement fabric for Film C. Mann Formulated Products (Easton, PA) Ease Release 200, supplied by Smooth-On (Easton, PA), was used as the release agent in this study. Table 1 shows the name, supplier, and average characteristic size, where applicable, for all the materials used in the films.

2.2. Film production

Table 2 shows the mass of each component used in the synthesis of the films. The base energetic reaction consisted of Al and MoO_3. The mass of $KClO_4$ was found using a percentage of the mass of the Al, MoO_3, and silicone binder. The solvent was excluded from the mass percent calculation due to the film being dried completely before testing. Film A contains 15% by mass $KClO_4$, where Film B and Film C have 30% $KClO_4$. These components are then sealed in a mixing vessel and set aside, while the binder–solvent system is prepared. The total mass of binder used in each film is listed in Table 2 and was mixed at the manufacturer's ratio of 10 parts A to 1 part B. The binder was then mixed by hand with an appropriate mass of xylene, seen in Table 2, to maintain constant percent solids in the slurry. 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 1:30 min. Total batch masses varied from 9246 mg for the Film A to 11,158 mg for Film B and Film C. The mixed slurry was placed in a vacuum chamber at 50.53 kPa of vacuum to de-aerate the slurry. The level of vacuum has to be carefully monitored to ensure that only the air is being pulled from the slurry. If the slurry is subject to vacuum in excess of 101.31 kPa of vacuum the solvent in the slurry will boil causing the slurry to foam. The slurry is then loaded into a blade casting machine designed and manufactured in house for energetic films. The blade casting machine is schematically shown in Fig. 1 and consists of a glass plate supported by a leveled aluminum base.

A layer of Mylar™ substrate is applied to the glass plate using a liquid wetting agent to ensure that the surface of the substrate is not wrinkled. Film A and Film C were cast with a coating of release agent applied to the Mylar™ substrate to allow easier removal of the finished film. Film B was cast on a Mylar™ substrate half coated length wise with a release agent to test the effect of the release agent on the flame speed. A micrometer adjustable blade, which allows easy changes in film thickness, was used to cast the films on the Mylar™ substrate at a constant 1 mm thickness. The slurry was poured onto the surface shown in Fig. 1 ensuring even coverage of the Mylar™. The coating machine draws the blade across the surface of the Mylar™ at a constant speed of 12.7 mm/s. Keeping the speed of the blade constant is important as variations in speed will cause variations in thickness of the coating. Film C was synthesized using an additive manufacturing approach where a 0.5 mm thick coating was cast and while still liquid the carbon fiber fabric reinforcement was laid onto the film. The carbon fiber fabric was lightly tamped until the slurry had flowed through the fabric to promote adhesion between the slurry and the carbon fiber fabric. A second layer of slurry was poured onto the carbon fiber fabric and the blade was drawn over this layer to generate the final film thickness of 1 mm.

To dry the film an acrylic box with evenly spaced holes is placed over the bed of the coating machine. This box ensures a consistent airflow over the entire film, which prevents cracking as the film cures. The film is allowed to cure for 24 h at room temperature, and is then peeled off the Mylar™ substrate and ready to be cut to size. The film is free standing and extremely flexible once cured. The silicone in the film provides support for the powdered energetic material, and as shown in Fig. 2, allows the film to be rolled or folded over on itself.

2.3. Combustion characterization

The slurry dries to form a film 50 mm wide, 100 mm long, and 1 mm thick. The samples were cut using a paper cutter to 6 mm wide by 50 mm long strip. To ensure repeatability four samples of each composition were examined and the flame speeds were measured. The
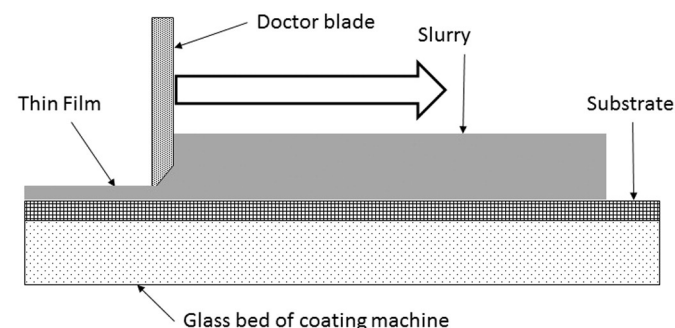
Table 1
Material properties and supplier information.

Material	Supplier	Average characteristic size (microns)
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
Carbon fiber fabric	ACP Composites (Livermore, CA)	N/A

Table 2
Mass of each component of film samples.

Mass (mg)/sample name	Al	MoO_3	$KClO_4$	Mold Max 30 silicone	Xylene
Film A	670.2	1790.7	707.7	3636.4	2441.7
Film B	670.8	1790.3	1523.3	4870.8	2417.0
Film C	670.4	1790.9	1523.6	4888.6	2840.3

Fig. 1. Schematic representation of blade casting machine.

Fig. 2. Photograph of flexible free standing energetic film being rolled onto itself.

uncertainty associated with the flame speed measurements is determined from the standard deviation of the four samples examined for each film and far greater than the uncertainty based on resolution of the diagnostic instrumentation. The films were placed on a ceramic pedestal and initiated with a butane igniter. Flame propagation was recorded at 250 frames per second at a resolution of 800 × 480 pixels using a Vision Research Phantom VII high speed camera. The videos were converted to a series of still images and these images were processed to find the horizontal position of the leading edge of the flame using National Instruments Vision Builder software. The reported flame speeds are the average flame speed for each composition.

2.4. Mechanical property testing

To prepare the samples for mechanical testing, the films were cut into strips 2.0 cm wide by 1.25 cm thick by 6.3 cm long. A SATEC Systems, Inc., Grove Ville PA, model 60HVL Universal Testing Machine was implemented to test the mechanical properties of the films. A custom apparatus made from four, $0.635 \times 3.80 \times 45$ cm steel straps was constructed to support the samples during testing. The prepared samples were loaded into the apparatus so that the majority of fibers were oriented along the axis of force, then clamped securely in place. A picture of this setup is shown below in Fig. 3. The samples were then

Fig. 3. Photograph of mechanical property testing apparatus.

pre-loaded until taut at which time a tensile load was applied at a rate of 444.8 N/min until the sample failed.

3. Results and discussion

Fig. 4 shows the average flame speed results for the films examined in this study with associated uncertainty. Film A burned the slowest of all the tested samples at $0.152 \pm .015$ cm/s, while Film B had the highest flame speed, $0.497 \pm .023$ cm/s. The addition of the reinforcement fabric slows the speed by 30% to $0.349 \pm .044$ cm/s.

Fig. 5 shows the position versus time plot for Film A. The sample was cut in such a way to ensure that only one half of the film would be in contact with the release agent when cast as shown schematically in Fig. 6. It can be seen in Fig. 5 that there is no change in the slope of the data on the graph. The linearity of the position versus time plot indicates that the use of the release agent will not affect the performance of the films.

Table 3 shows the maximum tensile load and the maximum stress, σ_{max}, for Film B and Film C reinforced. Film B failed upon initial loading causing the maximum load of 2.27 kg to be an estimate based on measurement errors at low loads. When the carbon fiber fabric is added to the film (i.e., Film C) the maximum load supported by the film is increased by approximately 3200%, to 72.35 kg.

4. Discussion

Fig. 3 shows that as $KClO_4$ wt.% increases, so does the flame speed of the film. The significant increase in flame speed could be attributed to the dominant mode of energy propagation. It has been reported by Farley et al. that $Al + KClO_4$ reactions exhibit low mass loss during reaction [17]. This means that negligible gas is generated by the reaction and the dominant mode of energy propagation is conduction. Since the films have few interior air voids, a conductively dominant reaction is going to transfer energy through the film more efficiently than a convectively dominant reaction. Also, $KClO_4$ could replace MoO_3 as the preferred oxidizer reacting with Al. If this is assumed, $KClO_4$ in Film A would only consume 367.5 mg of the approximately 670 mg present, leaving the remaining Al to react with MoO_3. Comparing theoretical heats of combustion (found using REAL code), the reaction between Al and $KClO_4$ (i.e., 9795.5 kJ/kg) produces significantly more energy than the reaction between Al and MoO_3 (i.e., 4401.9 kJ/kg). This comparison estimates that potentially half the Al in Film A is reacting with an oxidizer (i.e., MoO_3) that generates less energy than if Al was reacting with $KClO_4$. Film B and C contain enough $KClO_4$ to fully oxidize Al in the film with approximately 125 mg of oxidizer remaining and therefore lead to higher energy generation compared with Film A. The remaining oxidizer is then available to react with the silicone binder. This added heat from participation of the silicone binder
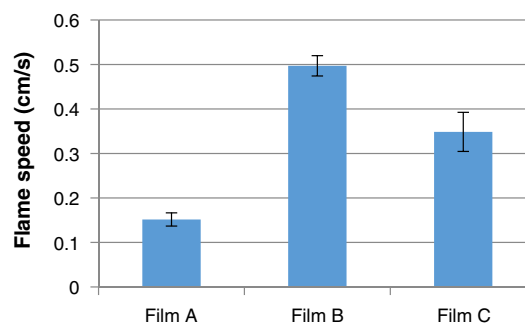

Fig. 4. Average flame speed for Film A (low $KClO_4$ concentration), Film B (high $KClO_4$ concentration); and, Film C (reinforced high $KClO_4$ concentration).
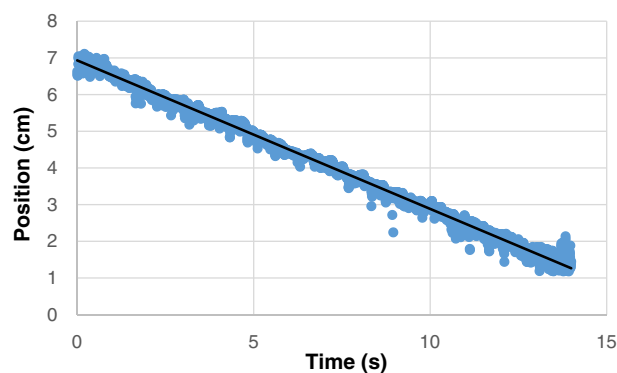
Fig. 5. Position versus time plot for Film B showing linearity of flame propagation.

would promote energy propagation and thus flame speed. In fact, Armstrong derived an expression relating flame propagation speed to thermal, physical and chemical properties of random particulate media assuming negligible gas production (i.e., conductively dominant energy propagation) and activation-energy asymptotic kinetics [18]. Assuming that thermal properties vary negligibly between Films A and B, the primary drivers for increased flame speed are combustion properties such as flame temperature, heat of combustion and activation energy. Film B potentially exhibits nearly twice the heat of combustion compared with Film A (based on thermal equilibrium calculations) and this correlates well with the observation that Film B also exhibits increased flame speed compared with Film A. It is further noted that silicone-based rubber reacting with $KClO_4$ has been documented such that incorporating a silicone binder in this study also provides a reactive medium to bind the reactant components into a continuous matrix and produce additional calorific output [19].

While Film B and Film C share similar masses of energetic components the flame speed for Film C is lower than Film B. This decrease in flame speed can be attributed to the introduction of the reinforcement fabric in Film C. Research on carbon reinforced polymer matrix composites to determine the flammability of the composites used in the aviation industry have been reported [20]. For example, Quintiere et al. show that carbon fiber is not flammable, but the resin encasing the carbon fiber fabric will begin to vaporize at 300 °C, and in the gas phase the resin will ignite and burn [20]. They further noted that while the resin was burning the carbon fiber fabric acted as insulation [20]. Due to this, the carbon fabric may act more like a heat sink in the reactive film absorbing energy generated by the reaction. This behavior is consistent with the decrease in flame speed associated with adding the reinforcement to the energetic film and establishes the feasibility of synthesizing structurally reinforced energetic films.

The inclusion of the reinforcement fabric in the film results in a dramatic increase in the maximum load supported by the film as expected. This results in an increase in σ_{max} of 17,740% when compared with the non-reinforced film. These results are consistent with other polymer matrix composites that have been studied. For example Rezaei et al. showed that reinforcement fabric significantly increased the strength of a base polymer matrix [16]. This is achieved by the fibers of the fabric supporting the load rather than the silicone binder which was shown to have very low strength without the reinforcement fabric.
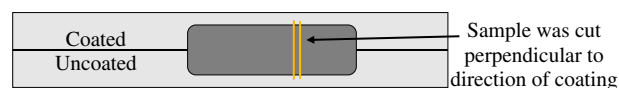
Table 3
Results from strength testing on Film B and Film C (reinforced).

	Maximum load (Kg)	σ_{max} (kPa)
Film B	2.27	861.84
Film C	72.3	168,420

5. Conclusions

In summary, a new method for synthesizing an energetic composite that is free standing and flexible has been shown. This method allows for single or multi-step casting that facilitates the introduction of solid additives such as reinforcement fabrics to the structure of the synthesized films. The addition of potassium perchlorate was shown to increase the flame speed of the film based on facilitating diffusion reaction mechanism via low gas generation and participating in the reaction. Since these films have limited air voids the energy released by the gas phase species from MoO_3 reaction is primarily lost to the environment. The effect of the release agent used during synthesis on the flame speed of the films was examined. Results show that the release agent has no effect on the flame speed of the film allowing this agent to be used to aid removal of the film from a substrate. Carbon fiber reinforcement fabric was used to strengthen the free standing energetic films which resulted in a 17,740% increase in σ_{max} of the film. This significant increase is attributed to the fabric supporting the applied load rather than the silicone binder which was shown to have low load bearing capabilities. While the reinforcement fabric enhanced the strength of the film the inclusion of this fabric caused a decrease in flame speed resulting from the carbon fiber fabric acting as a heat sink. While this method of synthesis allows manufacture of a flexible freestanding energetic film, the composition and rheology of the mixed slurry have potential as an extrusion cast energetic.

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Fig. 6. Schematic showing how Film B was cut to test effect of release agent on flame propagation.

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