Surface & Coatings Technology 284 (2015) 422–426

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

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

ARTICLE INFO

Article history:
Received 31 March 2015
Revised 24 May 2015
Accepted in revised form 24 May 2015
Available online 18 July 2015

Keywords:
Energetic materials
Mechanical properties
Strength testing
Blade casting
Tape casting
Additive manufacturing
Aluminum combustion
Thermites
Thin films
Energy generation

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.

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,

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

http://dx.doi.org/10.1016/j.surfcoat.2015.05.048
0257-8972/

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.

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

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

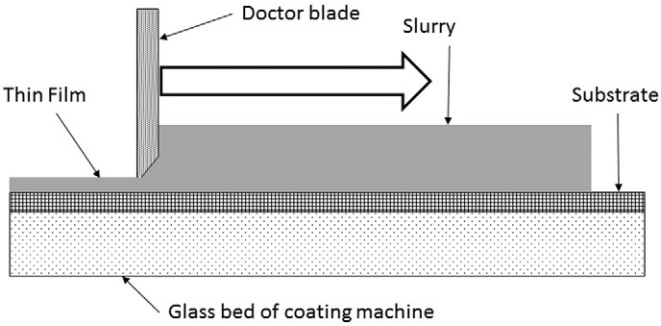

Fig. 1. Schematic representation of blade casting machine.