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Preparation and combustion of laminated iodine containing aluminum/polyvinylidene fluoride composites☆

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ABSTRACT

Energetic materials with a high iodine content and tunable reactivity are desirable for application as a biocidal agent. In this paper, aluminum/polyvinylidene fluoride (Al/PVDF) composites with different iodine content were prepared by an electrospray deposition method. Most of the iodine in the films are found to be fixed by PVDF and aluminum, which is released at 250 °C and 450 °C respectively. The heat release and burning rate of the iodine-containing films decreases with the increase of iodine content. With an iodine content of ≥40 wt.%, the film did not propagate. However, when fabricated in a laminate structure the threshold for iodine loading to sustain propagation increased to 67 wt.%. Evaluation of several multi-layered structured films indicated that an optimum single layer thickness of ~25 μm produced the fastest reaction velocity, with loadings of up to 67 wt.% iodine. The thermal decomposition and oxidation of the laminated Al/PVDF films are also investigated. It appears thus that iodine which acts as a reaction retardant can be loaded in higher concentrations if it is physically separated from the primary energetic. In so doing, the primary energetic can maintain a continuous ignition threshold to propagate and enable the heat released from reaction to evolve gas phase iodine.

1. Introduction

Weaponized bacterial spores such as *anthrax* require aggressive methods for their neutralization, either through exposure to strong bactericidal agents or application of heat. In some cases, it has been found that synergistic effects coupling both chemical and thermal effects work best. For example, exposure to high concentrations of hot iodine vapor has been shown to be effective [1,2]. To achieve high temperatures, energetic fuel/oxidizer formulations are common, and iodine can be introduced into the composites with iodine rich oxidizers. For example, I_2O_5, $NaIO_4/KIO_4$, $Cu(IO_3)_2/Bi(IO_3)_3/Fe(IO_3)_3/Ca(IO_3)_2/AgIO_3$ and iodine containing organic compounds are commonly used iodine-rich oxidizers for fuels such as Al and B [3–11]. Thermodynamically these formulations will nominally produce molecular iodine. However, some reactions such as $Al/NaIO_4$ (KIO_4) will produce iodides (NaI/KI) rather than iodine gas. An alternate approach is to simply add iodine in its elemental form to energetic formulations. Previously, we added elemental iodine into Al/CuO microparticle formulation to create a high iodine (50 wt.%) containing thermite [12]. Iodine has also been added to energetic formulation through ball milling with Al and B to create high iodine content composites [13,14]. Iodine-containing energetic materials generally (1) self-propagate with a large heat release; (2) have a high iodine content; (3) have long effective duration and are thus worthy of further exploration.

Currently, almost all iodine-containing energetic materials are powders, which need further processing such as pelleting before application. An alternative to these powders would be high iodine containing polymer composites. One such polymer fuel system Al/PVDF, which has high heat release, possesses good mechanical properties and has the potential for 3D printing [15]. The reactivity of Al/PVDF can be adjusted by controlling the composition, structure, and additives [16]. These advantages make it an ideal option to load iodine. In this study, elemental iodine was dissolved into an Al/PVDF precursor. And iodine containing free-standing films were prepared by electrospray deposition. The microstructure, thermal decomposition, iodine release and propagating speeds of these films were investigated. Employing a laminate structure, we find that Al/PVDF films can propagate with an iodine content as high as 67 wt.%.

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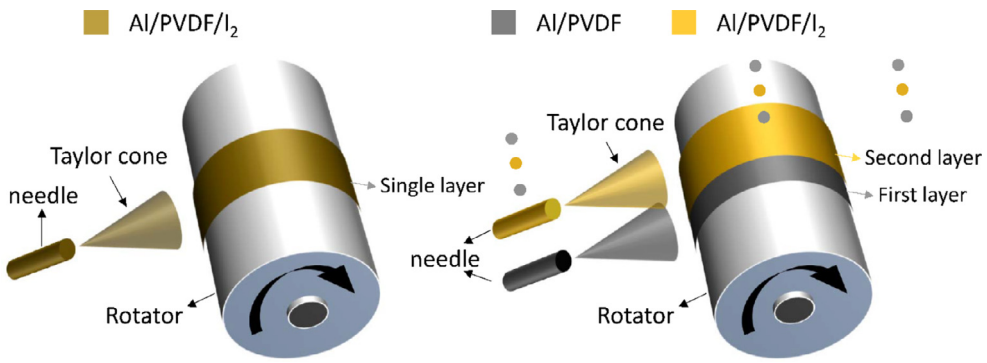

Fig. 1. Fabrication by electrospray deposition of single layered and multi-layered Al/PVDF/I_2 films.

2. Experimental section

2.1. Chemicals and precursors

Aluminum nanoparticles (Al NPs, ~85 nm) were purchased from Novacentrix. The active aluminum content is ~81 wt.% according to Thermogravimetry/Differential Scanning Calorimetry (TG/DSC) results. Polyvinylidene fluoride (PVDF, 534,000) and iodine (I_2, 99.8%) were purchased from Sigma-Aldrich. N, N-Dimethylformamide (DMF, 99.8%) was purchased from BDH chemicals. All chemicals were used as received. As example: for an Al/PVDF composite with 20 wt.% iodine, 150 mg PVDF was dissolved in 3 mL DMF, to which 50.55 mg of I_2 was added. Following dissolution, 52.2 mg Al NPs were then added into the solution and sonicated for 1 h. After stirring for 24 h, the suspension was ready for electrospray. For multi-layered films, there are two components. One is an iodine-containing component, and the other is the Al/PVDF. For a typical iodine containing part, 150 mg PVDF and 808.8 mg iodine was dissolved in 2.5 mL DMF, to which 52.2 mg Al was added. For Al/PVDF component, 150 mg PVDF was dissolved in 3 mL DMF and 52.2 mg Al was added. Al and PVDF are in stoichiometric ratio in all the cases.

2.2. Electrospray formation of Al/I_2/PVDF films with single and multi-layers

The details of the electrospray setup can be found in our previous studies [17,18]. In a typical setup a 10-mL syringe with stainless steel needle of inner diameter: ~0.43 mm was operated with a syringe pump. An electric field of ~3.3 kV/cm (for Al/PVDF) or ~5 kV/cm (for iodine containing Al/PVDF) was applied between needle and substrate. The distance between the needle and substrate was set as ~2 cm and the feed rate of precursor was set as ~2 mL/h. For the preparation of single layered Al/PVDF films, the precursor was sprayed without pausing. For the multi-layered films, after deposition of one Al/PVDF layer, electrospraying was paused for 5 min to allow the film to completely dry before the iodine continuing layer was sprayed as illustrated in Fig. 1. For these studies a 3-layer film has two Al/PVDF layers and one Al/PVDF/I_2 layer. For 5 layers there are three Al/PVDF layers and two Al/PVDF/I_2 layers.

2.3. SEM, EDS, XRD, FTIR and TG/DSC/MS

The microstructure of Al/PVDF films with iodine was investigated by using a Hitachi SU-70 scanning electron microscope (SEM) coupled to an energy dispersive spectrometer (EDS). The films were sectioned at low temperature by tweezers in liquid nitrogen and adhered to a carbon film on an SEM stage. The films were also characterized by powder X-ray diffraction (XRD, Bruker D8 with Cu K radiation) and attenuated total reflection (ATR) Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet i550R, Thermo Fisher Scientific), respectively. Thermogravimetry/differential scanning calorimetry/mass spectrometry (TG/DSC/MS) results were obtained with a TA Instruments Q600 and Discovery Mass spectrometer in an argon flow (100 mL/min) at a heating rate of 25 °C/min.

2.4. Burn rate measurement

To evaluate burn rate, the films were cut to 3 cm × 0.5 cm sections. The films were ignited with a Joule-heated nichrome wire (~1 cm in length, 0.010 in. in diameter) in a quartz tube filled with argon. After each run, the tube was cleaned, and then purged with a flow of argon for 5 min (flow rate: 10 L/min). Film burning was recorded using a high-speed camera at 14.9 μs per frame (Phantom V12.1; 256 × 256 pixels,). The average burn rate for each sample condition was evaluated in triplicate.

3. Results and discussion

Al/PVDF films with a fixed amount of Al/PVDF (~200 mg) and different iodine content of 5, 20, 35, 40, 45, and 50 wt.% were prepared. The SEM images and EDS results of the typical cross-sectional films are shown in Fig. 2. As the SEM images show, the thicknesses of the films with 5 and 20 wt.% are 40 and 50 μm, respectively. With further increase of iodine content to 50 wt.%, the thickness of the Al/PVDF film also increases to 90 μm. The SEM images also show morphology differences. Overall, most parts of the cross-sectioned films are smooth and dense. While at the higher iodine loadings, more cracking and delamination could be observed. As the EDS mapping images indicate, the mixing of iodine and PVDF (represented by fluorine) in all the samples is homogenous dispersed across the whole cross-section. However, the Al NPs appear to agglomerate with increased iodine content. The Al NPs disperse well in the film with 5 wt.% iodine but form concentrated regions on the micron scale when the iodine content ≥20 wt.%. Under imaging the iodine vaporized due to heating from the electron beam and formed bubbles as seen in the lower SEM image of 50 wt.% iodine loading case in Fig. 2. The corresponding elemental mapping is shown in Fig. 3a. From this Figure, we can mainly see the carbon (from PVDF), iodine, aluminum and fluorine (from PVDF). The gold (Au) is from the coating to avoid charging during SEM imaging. The iodine signal intensity of different films increases with the increase of iodine content. The crystalline structure of iodine containing films was also measured and compared to that of the Al/PVDF film without iodine, shown in Fig. 3b. The main species detected by XRD are aluminum and PVDF for both cases. The Al/PVDF film with 20 wt.% iodine shows only weak iodine peaks, indicating low crystallinity for iodine, and suggests that