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Ignition sensitivity and electrical conductivity of an aluminum fluoropolymer reactive material with carbon nanofillers

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ABSTRACT

The safe handling of powdered energetic material composites requires an understanding of their response to electrostatic discharge (ESD) ignition stimuli. In this study, a binary composite of aluminum (Al) and polytetrafluoroethylene (PTFE) is tailored for ESD ignition sensitivity by varying the concentration of highly electrically conductive nanofillers. The goal is to understand ESD ignition response of Al + PTFE when nanofiller loadings are added to the base mixture that negligibly affect combustion but significantly alter ignition and the electrical conductivity of the mixture. Previous work has shown a correlation between electrical conductivity and ESD ignition sensitivity. The nanofillers examined include carbon nanotubes (CNT), graphene nano platelets (GNP), and combinations of CNT and GNP. Adding CNT creates an electrical conductivity percolation threshold at a lower volume fraction compared to GNP. Hence, CNT are the controlling nanofiller that creates a percolating network when a combination of CNT and GNP are used. Various mixing methods are examined including sonication techniques and dry mixing. Results show that a composition insensitive to ESD ignition became sensitive by controlling its electrical conductivity through nanofiller addition.

1. Introduction

A pyrolant is an energetic mixture of solid fuel and oxidizer particles, a reactive combination that is highly exothermic upon ignition. This class of energetic materials enables tailoring reactants toward specific applications, unlike explosives whose reactivity is kinetically limited by the monomolecular crystal structure. Aluminum (Al) is a common fuel, and examples of oxidizers include metal oxides, other metals, or fluoropolymers such as polytetrafluoroethylene (PTFE). In fact, the use of PTFE as an oxidizer for reactions has been studied since the mid-1950s and found applications in flares, tracers, igniters, and propellants [1]. Kuwahara et al. compared the theoretical flame temperature of aluminum, magnesium, boron, and titanium mixed with PTFE and discovered that the composition with Al as the fuel produced a higher flame temperature (3764 K) than any of the other fuels [2]. Densmore et al. found similar results in measuring the temperature of the Al + PTFE reaction to reach as high as 3650 K [3].

Safe handling of energetic powders requires an understanding of their response to ignition stimuli. Powders are particularly prone to ignition from electrostatic energy. Weir et al. defined an electrostatic discharge (ESD) ignition sensitivity threshold of 100 mJ such that mixtures ignitable under 100 mJ are deemed ESD sensitive [4,5]. They also observed a correlation between electrical conductivity and ESD sensitivity; specifically, composites with a higher electrical conductivity such as aluminum (Al) + copper oxide (CuO) (i.e., >1000 nS/m) were ESD ignition sensitive and composites with a lower electrical conductivity such as aluminum + polytetrafluoroethylene (PTFE) (i.e., ~0.25 nS/m) were not ESD ignition sensitive [4].

The goal of this study is to understand the influence of highly electrically conductive nanofillers on ESD ignition sensitivity and electrical conductivity of Al + PTFE. An ideal nanofiller would be inert relative to the exothermic reaction and only a small percentage of the total mixture such that the overall combustion is not significantly altered but ESD ignition safety is improved. The objective

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is to increase the electrical conductivity of a pyrolant using nanofillers and locate a concentration-conductivity regime where ESD ignition may be observed. The addition of small quantities of conductive materials to a pyrolant significantly decreases the minimum ignition energy of the pyrolant, corresponding to a percolation threshold [6]. A percolation threshold corresponds to the concentration of nanofiller that produces a sharp increase in the overall electrical conductivity. However, percolation theory assumes that the system is homogeneous with random placement and orientation of fillers. Percolation threshold is a useful parameter for describing the connectivity of the conductive nanofiller in a sample [7–12] if it can be applied. If electrical conductivity is low, a percolation threshold may not be achieved and the nanofillers do not form a connected network through the sample. If electrical conductivity is high, nanofillers may form an interconnected network throughout the sample thereby producing orders of magnitude higher electrical conductivity than the mixture without nanofillers. A key factor in creating percolation is the dispersion quality of the nanofiller.

The Al + PTFE has a low electrical conductivity and is not sensitive to ESD when particle sizes are in the micrometer range [4,5]. Previous studies have shown that carbon nanofillers have a higher electrical conductivity and lower percolation threshold than carbon black, the standard material for adjusting electrical conductivity of many materials [12–15]. Therefore, the electrically conductive nanofillers examined here were carbon nanotubes (CNT) and graphene nano platelets (GNP). These nanofillers have high electrical conductivity and small concentrations are anticipated to affect the ESD ignition sensitivity of Al-PTFE. This objective was accomplished by mixing the formulations using various mixing procedures to optimize CNT and GNP dispersions. Samples were examined using scanning electron microscopy (SEM) to observe dispersion quality, and electrical conductivity was measured using established techniques. Although Al + PTFE is not ESD ignition sensitive when the Al particles have an average diameter in the micrometer regime [5], ignition was achieved for select samples that achieved a specified range for electrical conductivity.

2. Experimental

2.1. Materials

Aluminum (Al) powder has spherical particle diameters ranging from 3 to 4.5 μm and polytetrafluoroethylene (PTFE) powder has an average particle diameter of 35 μm; both were procured from Alpha Aesar. Multi-walled carbon nanotubes (CNT) and graphene nanoplatelets (GNP) were used as nanofillers and purchased from Alpha Aesar and Graphene Supermarkets, respectively. The CNT have an outer diameter of 3–20 nm, an inner diameter of 1–3 nm, and a length of 0.1–10 μm. The GNP flakes have a thickness of 8 nm with a length of 0.15–3.0 μm. It is important to note that pyrolants can be dangerous and must be handled with care and safety. The safe handling of these materials is nicely documented by Pantoya and Maienschein [16] with lessons and procedures for teaching student safety specific to an academic environment.

2.2. Mixing procedure

Equivalence ratio is defined as the ratio of the actual fuel/oxidizer ratio to the stoichiometric fuel/oxidizer ratio according to the Al + PTFE reaction shown in Eq. (1). Samples were prepared for an equivalence ratio equal to 1.0, i.e., for a stoichiometric reaction. A standard mixing procedure that combines powders using a hydrocarbon liquid (hexane) and sonicated to improve homogeneity of reactants was employed [17]. The hexane and powder solution was then poured into a Pyrex dish such that the hexane evaporates in the fume hood and Al + PTFE is reclaimed for further experimentation.

$$3C_2F_4 + 4Al \rightarrow 4AlF_3 + 6C \tag{1}$$

2.3. Adding CNT and GNP to AL + PTFE

The volume percent of the nanofillers along with their respective masses are listed in Table 1. The CNT, GNP, and combinations of CNT and GNP were mixed with Al + PTFE in various concentrations. The nanofiller mass was determined by first considering the sample volume of Al + PTFE and calculating the bulk density or percent of the theoretical maximum density (TMD) of the Al + PTFE as shown in Eq. (2)

$$\mathrm{TMD} = \frac{1}{\sum_{i=1}^{N} \frac{m_i}{\rho_i}} \tag{2}$$

In Eq. (1), m is the mass fraction of reactant species i and ρ is the density of species *i*. The TMD for Al + PTFE is 1.73 g/cc. The mass of the nanofiller was calculated using a volumetric percentage of Al + PTFE and the density of the nanofiller. Three different mixing methods were used to optimize dispersion of the nanofillers in Al + PTFE.

2.3.1. Short sonication mixing procedure

An aqueous dispersant (Alfa Aesar, no. 44276) for multi-walled CNT was used to make a good dispersion in water. The nanofillers were added to a solution of 0.075 mL dispersant in 25 mL of water; this mixture was then sonicated for 1 min to form the nanofiller dispersions. The Al + PTFE was mixed with isopropyl alcohol and added to the dispersions and again sonicated for 1 min. After sonication, the solvents were evaporated off, leaving a dry mixture of Al + PTFE and CNT and GNP nanofiller.

2.3.2. Long sonication mixing procedure

The CNT and GNP nanofillers were sonicated in distilled water for 30 min which allowed for a complete dispersion in the solvent (i.e. no settling of nanofiller was visible in solution). The dispersed solution was then sonicated for 1 min and the solvent evaporated. During evaporation, the Al + PTFE settled on the bottom of the solution and separated itself from the dispersed CNT and GNP nanofiller, which settled on top of the Al + PTFE. The dry powders were dry mixed as they were collected and placed in a storage container.

Table 1
Percent of nanofiller and mass for CNT, GNP, 1 vol.% of GNP/CNT combination, and 2 vol.% of GNP/CNT combination.

CNT		GNP		1 vol.% GNP/CNT			2 vol.% GNP/CNT		
Vol.% added (%)	Mass (mg)	Vol.% added (%)	Mass (mg)	Ratio of GNP/CNT	Mass GNP (mg)	Mass CNT (mg)	Ratio of GNP/CNT	Mass GNP (mg)	Mass CNT (mg)
0.20	1.8	0.50	5.6	20/80	2.2	7.1	20/80	4.5	14.3
0.50	4.5	1.00	11.2	40/60	4.5	5.4	40/60	8.9	10.7
1.00	8.9	2.00	22.4	60/40	6.7	3.6	60/40	13.4	7.2
2.00	17.9	3.00	33.5	80/20	8.9	1.8	80/20	17.9	3.6
		4.00	44.7						