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Thermal investigations of nanoaluminum/perfluoropolyether core–shell impregnated composites for structural energetics

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ABSTRACT

An operationally simple blendable approach to producing structural energetic composites loaded with nanoaluminum (n-Al) particles coated by perfluoropolyethers (PFPE) yields shape moldable, structurally flexible materials. The epoxide system of poly(ethylene glycol) diglycidyl ether (PEG-DGE) and triethylenetetramine (TETA) are partially cured with an energetic blend of n-Al/PFPE core–shell particles and mechanically mixed and produce a homogeneous composite material whereby energetic potency is indefinitely shelf-stable. The composites are characterized by a suite of thermal techniques using DSC, TGA, and SDT in addition to open flame burn rate and heat of combustion measurements. This composite system may further expand the use of energetic materials with tailorable exothermic properties.

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1. Introduction

The development of novel energetic structural composites is an area of growing interest for both military and commercial applications [1]. Energetic materials are often engineered to be stable and structurally robust yet exothermically decompose under programmable conditions such as at a specific temperature, upon impact, or when exposed to other energy stimuli. Composites are an ideal selection for the design of a structural energetic material because they provide reactive reinforcements in a non-reactive host polymer-matrix material. Often the reactive reinforcements in these systems are metal fuel-oxidizer combinations that undergo an oxidation–reduction thermite reaction releasing energy. Advances in the field have generated diverse material platforms ranging from bulk components to fibers [2–8].

In general, energetic materials exothermically ($\Delta H < 0$) and spontaneously ($\Delta G < 0$) react. High explosives detonate at supersonic speeds and propellants and pyrolants react on much slower time scales [9]. Propellants undergo deflagration reactions at subsonic speeds and pyrolants burn at even slower subsonic speeds (i.e., ~10 cm/s). Examples of high explosives include TNT ($C_7H_5N_3O_6$), PETN ($C_5H_8N_4O_{12}$), and HMX ($C_4H_8N_8O_8$) [10]. Gun and rocket propellants like black powder, liquid fuels and oxidizers, and composite fuels are examples of propellants [11]; pyrolants are usually fuel rich and are constituted from metallic or non-metallic fuels with inorganic/organic oxidizers or alloys. Related to the interest of this work, the classic example of magnesium–polytetrafluoroethylene (PTFE or Teflon®)-vinylidene fluoride (Viton®), commonly referred to as MTV, remains one of the most famous and still widely-used metal-fluorocarbon based pyrolant formulations [12]. This area of fluorocarbon-based oxidizers and metal fuels continues to garner interest and has been consolidated in a recent account [13]. Very recent examples from Pantoya et al. have developed numerous energetic materials based on metallized Teflon® formulations [14–18].

Previously, we reported a metallized energetic composite by doping the epoxide system, diethylenetriamine (DETA) polymerized with bisphenol A diglycidylether (BADGE), with a blend of n-Al/perfluoropolyether (PFPE, commonly referred to as Fomblin®) core–shell (fuel/oxidizer) particulate fillers to yield a structurally rigid material [19]. The resulting epoxide composite could be exothermically decomposed at a specific temperature by changing the loading and composition of the n-Al/PFPE blend which was quantified by XRD powder diffraction. PFPEs are well known to decompose at

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lower temperatures in the presence of native metals thereby allowing for the design of an energetic material that would decompose at a prescribed temperature [20–22]. To our knowledge, unlike most fluorocarbon-based energetic systems, this was the first blended system to demonstrate the use of a liquid oxidizer (the PFPE) which promotes intimate contact with the metal fuel. Based on our initial findings from this previous research which has expanded to energetic metallized electrospun fibers [23], we were interested in producing a mold-shapeable, flexible epoxide system in order to expand the type of materials available for structural energetic use. Elastomeric materials could be highly valuable to the energetic community because rigid materials have limited applicability and use. A flexible, structural energetic component can sustain additional stresses without or before damage to the part as a whole and expands the scope of application. Poly(ethylene glycol) diglycidyl ether (PEG-DGE) and triethylenetetramine (TETA) are chosen as starting materials due to their ability to form a flexible, solvent swelled network material. The PFPE Fomblin® Y is blended with n-Al particles to produce an energetic blend that is then loaded in the PEG-DGE/TETA epoxy composite producing a novel structural energetic composite. The use of a PFPE is also employed to take advantage of the hydrophobic properties of PFPEs in hopes of creating a composite that is impermeable to moisture and air, ultimately increasing shelf life. In this study, a new structural energetic composite is fabricated and expanded details of thermal properties and their correlations include thermal decomposition, open flame burn rates, and heat of combustion.

2. Experimental

2.1. Materials

Triethylenetetramine (TETA, 60%), poly(ethylene glycol) diglycidyl ether (PEG-DGE, avg. mol wt 500 g/mol), and the perfluoropolyether (PFPE) (Fomblin® Y LVAC 25/6, avg. mol wt 3300 g/mol) were all purchased from Sigma–Aldrich and were used as received without any further purification. The nanometer-sized aluminum (n-Al) powder was obtained from the US Army Armament Research, Development, and Engineering Center (ARDEC) and has an average particle size distribution of 80 nm, as determined by TEM from the supplier. The manufacturer found the aluminum to be ca. 70% active as determined by TGA analysis by measuring the mass gain due to oxidation.

2.2. n-Al/PFPE core–shell blend preparation

A 30 wt% blend of n-Al/PFPE is prepared according to the method described in previous studies and is briefly summarized here [19]. Typically prepared in 1 g batches, 30 wt% n-Al was mixed with PFPE in a glove box, removed from the inert atmosphere, vortexed for 1 min and then used for composite preparation.

2.3. PEG-DGE/TETA epoxy resin preparation

The preparation of composites has been reported previously [19]. Optimized epoxy resin formulations were produced by mixing PEG-DGE (3.60 g, 6.84 mmol, 90 wt%) and TETA (0.40 g, 2.74 mmol, 10 wt%). Resulting casted pucks are cured at room temperature on the bench top for 24 h producing an optically transparent, flexible solid.

2.4. PFPE/PEG-DGE/TETA composite preparation

The PEG-DGE/TETA formulation is allowed to partially cure (A-stage cure) in open air at room temperature for 15 h before adding various loadings of PFPE (5–10 wt%). After addition of the PFPE, the entire mixture is stirred for 5 min and fully cured (B-stage cure) in open air at room temperature for an additional 24 h producing a white, homogeneous, flexible solid.

2.5. n-Al/PFPE/PEG-DGE/TETA composite preparation

PEG-DGE/TETA formulation is allowed to partially cure (A-stage cure) before adding various loadings of the 30 wt% n-Al blended in PFPE (6, 10, and 20 wt% n-Al/PFPE loading in epoxy matrix). After addition of n-Al/PFPE, the composite is stirred for 5 min and fully cured (B-stage cure) in open air at room temperature for 24 h producing a dark gray, flexible composite.*Potential hazard note*: In our studies, the preparation of n-Al/PFPE blends and resulting composite formulations showed indefinite shelf-stability in open air and during physical handing of the materials. These materials are/should be prepared on small-scale batches. However, we stress caution in handling these materials by using the proper personal protection equipment (gloves, safety glasses, and flame retardant clothing). Avoid exposing materials to an open flame, direct heating, or other energy point sources (unless under controlled conditions and by an individual experienced in the art) as these formulations have not been fully tested.

2.6. Thermal characterization

All thermal analysis experiments are performed in nitrogen taken from the head space on a liquid nitrogen tank that first passes through Drierite and all sample sizes are ca. 5–10 mg. TA Universal Analysis 2000 graphical software is used to determine the temperature of all thermal events and calculate remaining amounts of samples.

Differential scanning calorimetry (DSC) was performed on a TA Auto Q20 Instrument. Samples are sealed in aluminum hermetic pans with an empty sealed hermetic pan serving as the reference. Two different heating programs are used to probe different thermal transitions. The first program is used to heat treat as prepared samples which are cooled from room temperature to −80 °C and are then heated to 350 °C at a rate of 5 °C/min in order to report the untreated glass transition (T_{g1}) and cure (T_{cure}) temperatures. The heat treated samples are cycled twice from room temperature to −80 °C and heated to 150 °C at a rate of 5 °C/min. On the third cycle, samples are heated to a final temperature of 350 °C. Heat treated thermal transitions of T_{g2}, pre-ignition reaction (T_{PIR}), and maximum (T_{max}) temperatures are reported on the third cycle.

Thermal gravimetric analysis (TGA) was performed on a TA Q500 instrument at a scan rate of 5 °C/min. The epoxy formulations are heated in a platinum crucible and heated from room temperature to 900 °C. TGA is used to determine decomposition temperatures (T_d) and remaining mass balances/char yields (%) of decomposed samples.

Simultaneous differential thermogravimetric/calorimetry analysis (SDT) was performed on a TA Q600 instrument. Samples are measured into a platinum crucible with an empty platinum crucible serving as the reference. Samples are heated from room temperature to 800 °C at a rate of 5 °C/min.

2.7. Burn rate determination

Quantitative burn tests are performed on all samples to determine burn rates in air. Bulk samples (ca. 150 mg) with dimensions ca. 12 mm × 2 mm × 8 mm are cut from each fully cured puck. The flame from a propane torch is exposed to the sample held by metal tweezers for 10 s and removed upon which the ignited samples burn until the flame is extinguished leaving